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INORGANIC AND ANALYTICAL CHEMISTRY

PEROXY COMPOUNDS OF ZIRCONIUM AS PRODUCTS OF THE INTERACTION OF THE HYDROXIDE WITH HYDROGEN PEROXIDE

S. Z. Makarov and L. V. Ladeinova

The N. S. Kurnakov Institute for General and Inorganic Chemistry, Academy of Sciences
of the USSR

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In a previous literature review [1] of the peroxy compounds of the elements titanium, zirconium, and cerium in the tetravalent state, we stated that zirconium can form the so-called zirconium hydroperoxide $Zr(OOH)(OH)_3$ [2], of over-all composition $MeO_3 \cdot 2H_2O$ [3-7]. There is no information in the literature as to other peroxy compounds of zirconium. In the present paper we have investigated the interaction of zirconium hydroxide with aqueous solutions of hydrogen peroxide at concentrations up to 90-96.5%, at 0 and 20°. We have been able to characterize more completely the interaction of the active form of $Zr(OH)_4$ with H_2O_2 , to establish limits for the existence of zirconium peroxy compounds, and to obtain the new compounds $ZrO(OOH)(OH)$ and ZrO_3 in addition to the fully authenticated $Zr(OOH)(OH)_3$.

EXPERIMENTAL

The hydroxide of tetravalent zirconium was prepared in the form of an amorphous powder as follows: A solution of the nitrate of tetravalent zirconium (4.25 g) was treated, with stirring, with an excess of ammonia solution ($d = 0.985$). The white-colored gelatinous precipitate of zirconium hydroxide was filtered off, well washed with distilled water, and dried in vacuo at 30°. The dry product was finely ground and used in this form for investigation.

A thermal analysis curve of this material (Fig. 1) was characterized by an endothermic effect at 100-120°, associated with dehydration of the hydroxide, and an exothermic effect at 410-443°, due to conversion of the amorphous to a crystalline form. Pure hydrogen peroxide, without stabilizer, was prepared by distillation of perhydrol in vacuo. The active oxygen in our products was determined by titration with 0.1 N $KMnO_4$ in the presence of sulfuric acid.

Zirconium was determined by two gravimetric methods. When a solution was used containing less than 40% of H_2O_2 , the product containing zirconium peroxide was first dried, ignited to ZrO_2 in a muffle at 800-900°, cooled, and weighed. When a stronger hydrogen peroxide solution was used, the product was first dissolved in sulfuric acid and precipitated with ammonia. This precipitate was then filtered off, dried, and ignited to ZrO_2 in a muffle at 800-900°.

It should be noted that the solubility of zirconium hydroxide in hydrogen peroxide solution is extremely low (for water the solubility product of $Zr(OH)_4$ is $8 \cdot 10^{-52}$), so that zirconium was not determined in the liquid phase.

Interaction of Zirconium Hydroxide with Hydrogen Peroxide at 0 and -20°

The study of the process of interaction of $Zr(OH)_4$ with H_2O_2 solution was carried out by the usual solubility method, and the results were expressed graphically in a $ZrO_2-H_2O-\frac{1}{2}O_2$ diagram. The classical method of residues was sufficiently reliable to determine the actual composition of the peroxide phases formed, and to establish the concentration limits for their existence in hydrogen peroxide solutions. The minimum time taken to establish equilibrium between the chemical compositions of the liquid and solid phases was found to be 1.5 to 2 hr, as is well shown in Fig. 2. The interaction of $Zr(OH)_4$ with hydrogen peroxide solutions was investigated at 0 and -20°; the results are shown in Tables 1 and 2 and in Figs. 3 and 4.

Table 1 and Fig. 3 show that, at 0°, three solid phases can be present: the original $Zr(OH)_4$ and two peroxides (hydroperoxides to be precise) of over-all compositions $ZrO_3 \cdot 2H_2O$ and $ZrO_3 \cdot H_2O$. The compound $ZrO_3 \cdot H_2O$ is formed as a dehydration product of $ZrO_3 \cdot 2H_2O$ in concentrated hydrogen peroxide solutions. The limits of existence of these solid phases at 0° are shown in Table 3.

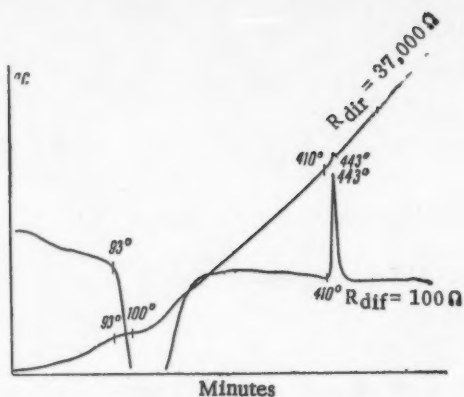


Fig. 1. Thermal analysis curve of zirconium hydroxide.

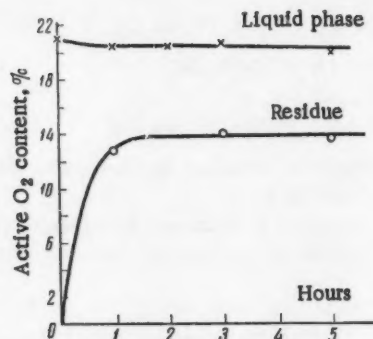


Fig. 2. Time for establishment of equilibrium in the system $Zr(OH)_4-H_2O_2-H_2O$ at 0° .

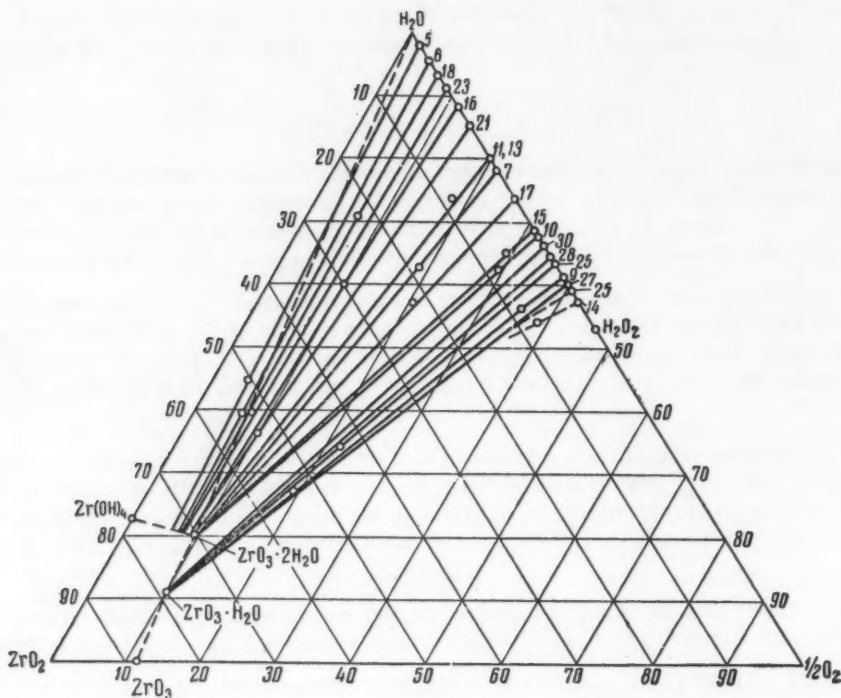


Fig. 3. Isotherms at 0° for the ternary system $Zr(OH)_4-H_2O_2-H_2O$.

There was considerable decomposition with H_2O_2 contents greater than 80% in the liquid phase.

The results obtained at -20° were more complicated. Ice crystallizes from the $H_2O-H_2O_2$ system with H_2O_2 concentrations up to 27.64%, and $ZrO_3 \cdot H_2O$ is formed in the liquid phase together with the original $Zr(OH)_4$; as at 0° , $ZrO_3 \cdot H_2O$, the phase corresponding to the first stage in dehydration of $ZrO_3 \cdot 2H_2O$, is also formed; finally, ZrO_3 is produced when the H_2O_2 concentration in the liquid phase is greater than 92%. Table 4 shows the concentration limits for the existence of these phases at -20°

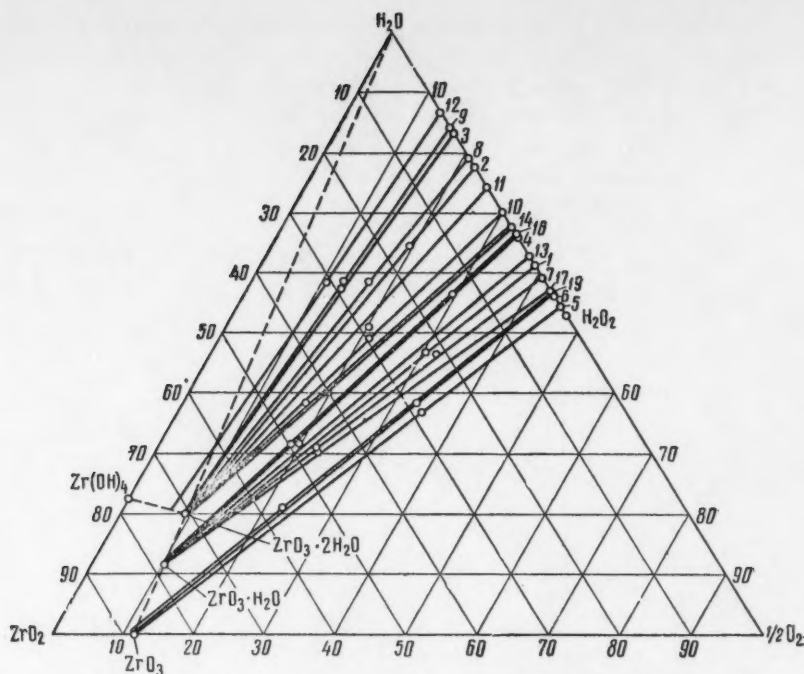


Fig. 4. Isotherms at -20° for the ternary system $\text{Zr(OH)}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$.

TABLE 1. Data for the Interaction of Zr(OH)_4 with H_2O_2 Solutions at 0°

Expt. No.	Composition of liquid phase, % w/w		Composition of residue, % w/w		Solid phase
	O_2 active	H_2O_2	O_2 active	ZrO_2	
5	1,99	4,23	4,76	50,03	$\text{Zr(OH)}_4 + \text{ZrO}_3 \cdot 2\text{H}_2\text{O}$
6	4,16	8,84	5,87	44,72	The same
18	6,81	14,48	6,50	22,27	"
4	8,61	18,29	6,14	54,07	"
23	8,97	19,05	7,67	52,21	"
16	11,52	24,49	10,02	29,62	$\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$
21	14,62	31,08	10,00	53,72	The same
11	19,71	41,90	19,15	6,13	"
13	19,97	42,45	17,91	8,42	"
7	21,27	45,22	13,21	13,95	"
19	21,90	46,56	18,39	18,57	"
17	26,20	55,72	21,91	22,23	"
15	31,12	66,16	29,17	6,00	"
10	31,67	67,52	29,23	8,02	"
30	33,83	71,92	20,80	49,93	$\text{ZrO}_3 \cdot \text{H}_2\text{O}$
25	36,34	77,25	22,56	43,55	The same
9	38,51	81,87	35,52	8,90	"
27	39,10	83,13	19,15	53,25	"
29	40,75	86,63	21,76	41,79	Decomposed
14	42,34	90,01	38,91	8,14	"

When the attempt was made to isolate the residues corresponding to the solid phases $\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$, $\text{ZrO}_3 \cdot \text{H}_2\text{O}$, and ZrO_3 , and to separate them from their mother liquors by such means as washing with alcohol and ether or drying in vacuo at room temperature (using normal preparative methods), the products showed a very marked loss in active oxygen content as the result of decomposition (Table 5). This fact gives some reason for believing that the peroxy compounds of zirconium cannot be considered as hydrates of ZrO_3 .

TABLE 2. Data for the Interaction of $Zr(OH)_4$ with H_2O_2 Solutions at -20°

Expt. No.	Composition of liquid phase, % w/w		Composition of residue, % w/w		Solid phase
	O_2 active	H_2O_2	O_2 active	ZrO_2	
12	13,00	27,64	10,94	30,93	$Zr(OH)_4 + ZrO_3 \cdot 2H_2O$
9	16,00	34,02	12,83	28,03	$ZrO_3 \cdot 2H_2O$
24	16,25	34,55	12,97	28,90	The same
3	16,50	35,08	13,14	29,32	"
8	20,86	44,35	16,43	24,42	"
2	22,05	46,88	19,75	15,93	"
11	25,52	54,26	20,32	28,73	"
10	29,52	62,76	21,38	29,21	"
15	31,74	67,48	17,46	46,11	"
14	32,08	68,20	17,73	43,96	"
16	33,37	70,94	18,65	49,47	$ZrO_3 \cdot H_2O$
4	33,54	71,30	29,60	14,05	The same
22	35,65	75,79	21,84	39,10	"
25	36,22	77,00	23,21	37,00	"
13	37,09	78,85	19,20	48,32	"
1	38,55	82,00	31,25	22,71	"
7	40,87	86,90	31,67	25,95	"
17	42,86	91,12	22,14	46,48	"
6	43,71	92,93	35,05	28,28	ZrO_3
19	43,87	93,27	22,40	56,03	ZrO_3
20	45,00	95,67	23,58	55,90	The same
5	45,37	96,45	34,04	28,42	"
21	45,38	96,48	22,15	58,30	"

TABLE 3. Concentration Limits for the Existence of Solid Phases in the System $Zr(OH)_4-H_2O_2-H_2O$ at 0°

Solid phase	H_2O_2 concentration, % w/w	
	lower limit	upper limit
$Zr(OH)_4$	4,23	19,05
$ZrO_3 \cdot 2H_2O$	19,05	71,92
$ZrO_3 \cdot H_2O$	71,92	83,13

TABLE 4. Concentration Limits for the Existence of Solid Phases in the System $Zr(OH)_4-H_2O_2-H_2O$ at -20°

Solid phase	H_2O_2 concentration, % w/w	
	lower limit	upper limit
Лед	0,00	27,64
$Zr(OH)_4$	27,64	34,02
$ZrO_3 \cdot 2H_2O$	34,02	70,94
$ZrO_3 \cdot H_2O$	70,94	92,93
ZrO_3	92,93	96,45

TABLE 5. Dehydration Data for the "Residues" $ZrO_3 \cdot 2H_2O$, $ZrO_3 \cdot H_2O$, and ZrO_3

Residue, corresponding solid phase	Product composition, % w/w			
		O_2 active	ZrO_2	H_2O
$ZrO_3 \cdot 2H_2O$ washed with alcohol and ether	Initial	13,78	41,10	45,12
		5,11	70,32	24,57
$ZrO_3 \cdot H_2O$ washed with alcohol and ether	Initial	23,21	37,00	39,79
		5,41	70,84	23,75
ZrO_3 washed with alcohol and ether, dried in vacuo at 20°	Initial	29,20	40,75	30,05
		4,30	75,56	20,14

Differential Heating Curves of the Solid Phase Residues $ZrO_3 \cdot 2H_2O$, $ZrO_3 \cdot H_2O$, and ZrO_3

The heating curves were obtained with a recording Kurnakov pyrometer, using a Pt-PtRh thermocouple, at a heating rate of $3-4^\circ$ per min, simultaneously with a record of the volume of oxygen evolved, for the different residues (Table 6).

TABLE 6. Data for the Chemical Compositions of the Liquid Phases and "Residues" Corresponding to the Solid Phases $\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$, $\text{ZrO}_3 \cdot \text{H}_2\text{O}$, and ZrO_3

Solid phase	Residue composition, % w/w			Liquid phase composition, % w/w	
	ZrO ₂	O ₂ active	H ₂ O	O ₂ active	P ₂ O
$\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$	28,90	12,97	58,13	16,25	83,75
$\text{ZrO}_3 \cdot \text{H}_2\text{O}$	39,10	21,84	39,06	35,65	64,35
ZrO_3	55,90	23,58	20,52	45,00	55,00

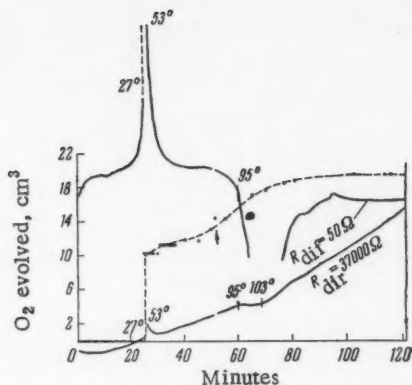


Fig. 5. Heating curves for the residue corresponding to $\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$.

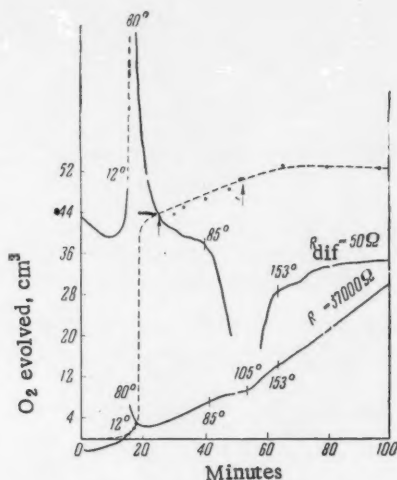


Fig. 6. Heating curves for the residue corresponding to $\text{ZrO}_3 \cdot \text{H}_2\text{O}$.

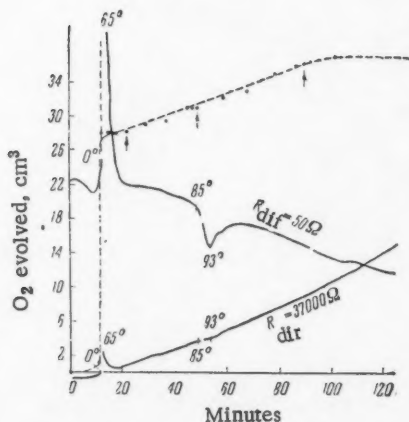
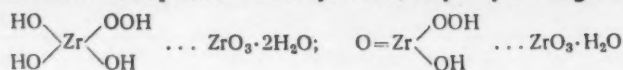


Fig. 7. Heating curves for the residue corresponding to ZrO_3 .

The heating curves obtained are shown in Figs. 5-7. The differential heating curves are similar in form, and are characterized by pronounced exothermic and endothermic effects. The position of the exothermic effect corresponds in time with the start of an intense oxygen evolution (the dotted curve). In this investigation we used the "residues," i.e., the solid phases not freed from mother liquor, with excess of hydrogen peroxide of different concentration, so that the thermal decomposition of hydrogen peroxide may have contributed to this first effect. However, analysis carried out to interpret the thermal effects showed that this exothermic effect does correspond to the main decomposition reaction of the zirconium hydroperoxides. Thus, the reaction $\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$ or $\text{Zr}(\text{OOH}(\text{OH}))_3 \rightarrow \text{Zr}(\text{OH})_4 + \frac{1}{2}\text{O}_2$ begins at 27° , and $\text{ZrO}_3 \cdot \text{H}_2\text{O}$ or $\text{ZrO}(\text{OOH})(\text{OH}) \rightarrow \text{ZrO}(\text{OH})_2 + \frac{1}{2}\text{O}_2$ begins at 12° , while,

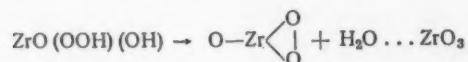
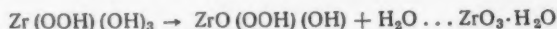
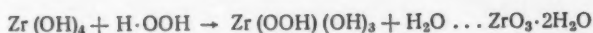
in view of the obvious effect of excess H_2O_2 , ZrO_3 decomposition begins at 0° . Further oxygen evolution in the thermal breakdown of the products is associated with decomposition of excess hydrogen peroxide, and this exothermic effect to a considerable extent runs parallel to the endothermic effect of $\text{Zr}(\text{OH})_4$ dehydration to $\text{ZrO}(\text{OH})_2$. It is natural that this endothermic effect occurs close to $85\text{--}95^\circ$ for all three products.

Thus, in the course of a study of the interaction of zirconium hydroxide with hydrogen peroxide at 0 and -20° , phases were obtained of over-all composition $\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$, $\text{ZrO}_3 \cdot \text{H}_2\text{O}$, and ZrO_3 . From the behavior of the first two products, with regard to thermal decomposition and dehydration, they may be assigned hydroperoxide structures:



ZrO_3 may be written as $\text{O}=\text{Zr} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$.

The chemical reactions corresponding to their formation from $\text{Zr}(\text{OH})_4$ and H_2O_2 may be written:



ZrO_3 is a typical peroxide compound.

SUMMARY

1. A study has been made of the interaction of $\text{Zr}(\text{OH})_4$ with H_2O_2 under isothermal conditions at 0 and -20° . Three peroxy phases were obtained in addition to $\text{Zr}(\text{OH})_4$: $\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$, $\text{ZrO}_3 \cdot \text{H}_2\text{O}$, and ZrO_3 .

2. Experiments on the dehydration and differential thermal analysis of the residues corresponding to these solid phases indicated that $\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{ZrO}_3 \cdot \text{H}_2\text{O}$ can be considered as the hydroperoxides $\text{Zr}(\text{OOH})(\text{OH})_3$ and

$\text{ZrO}(\text{OOH})(\text{OH})$, while ZrO_3 is the peroxide type compound $\text{O}=\text{Zr} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$.

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PEROXY COMPOUNDS OF CERIUM

S. Z. Makarov and L. V. Ladeinova

The N. S. Kurnakov Institute for General and Inorganic Chemistry, Academy of Sciences of the USSR

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There is not very much information in the literature on peroxy compounds of tetravalent cerium, which are usually considered in connection with the properties of peroxy compounds of titanium and zirconium. Cerium peroxides have been obtained by the interaction of Ce^{4+} salts with aqueous solutions of hydrogen peroxide and ammonia [1-6], by the direct interaction of $Ce(OH)_4$ with H_2O_2 [5-7], and, finally, by self-oxidizing reactions from cerium salts [8-13]. The compounds obtained by most investigators [2, 6, 14-16] have usually been represented by the general formula $CeO_3 \cdot 2H_2O$, and only in a few papers [7, 15, 17-19] have they been considered as hydroperoxides of the type $Ce(OOH)(OH)_3$.

In the present work, we have differed from previous investigators in synthesizing cerium peroxy compounds using highly concentrated hydrogen peroxide (up to 98%). By this use of highly concentrated hydrogen peroxide, by lowering the temperature to -20° , and by applying the classical solubility method and the graphical method of residues for analysis, we have been able to synthesize new, previously unknown peroxy compounds, in addition to $CeO_3 \cdot 2H_2O$.

EXPERIMENTAL

The starting material was the salt $Ce(SO_4)_2$. Precipitation with ammonia gave the hydroxide $Ce(OH)_4$, and this was carefully washed to give a porous yellow product of high activity. The washed product was dried in vacuo at about 40° and ground up to a fine powder. The quality of the $Ce(OH)_4$ obtained was of considerable importance. On keeping, it "aged," lost its activity, and became unsuitable for investigation. The differential heating curve of $Ce(OH)_4$ was characterized by an endothermic effect at $115-155^\circ$, associated with dehydration to CeO_2 . The hydrogen peroxide was used without stabilizer; it was prepared by distillation of perhydrol in vacuo. The cerium content, if high enough, was determined by the normal persulfate method of titration to Ce^{3+} with ferrous ammonium sulfate. Since we used the solubility method for synthesis, it was necessary to analyze the liquid phase together with the so called "residue;" but the former was only analyzed for its content of active oxygen in a sulfuric acid medium, because the solubility of $Ce(OH)_4$ is very low in aqueous solution. The solubility product of $Ce(OH)_4$ is $2 \cdot 10^{-48}$.

It should be noted that we were obliged to abandon the methods normally recommended for determining active oxygen in cerium peroxy compounds (Pisarzhevskii [6], Kleve [2], Schwarz and Glese [15]). With H_2O_2 concentrations greater than 20%, these methods gave very unreliable results, and we therefore used a volumetric method for determining active oxygen, with complete thermal decomposition of the "residue." This determination was carried out with the apparatus shown in Fig. 1. The container A, previously cooled, was charged with a sample of the moist cerium peroxide (the so-called "residue") and rapidly connected to the ground joint B, which carried a calcium chloride tube to remove water. The gas evolved by decomposition of the cerium peroxide was collected in the buret C, which was surrounded by a water jacket whose temperature could be read on the thermometer D. The volume of gas evolved was measured and corrected to normal temperature and pressure, and the active oxygen content of the sample could then be calculated as a percentage. The apparatus was carefully checked for leaks before each measurement. This method gave satisfactory results provided that a correct measurement was made of the total volume of oxygen evolved in the decomposition of the cerium peroxide.

Peroxy compounds of cerium, enriched with highly concentrated hydrogen peroxide, are relatively unstable. There was thus a possibility of loss in active oxygen during weighing of the sample. It was therefore more convenient to determine the weight of the sample precisely from the weight of the residue after decomposition, the increase in weight of the calcium chloride tube, and the calculated weight of the corrected volume of oxygen evolved on decomposition. Comparison of the results of active oxygen determination in cerium peroxy compounds by different

methods showed that as long as the compound formed was $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$, the Pisarzhevskii method gave results agreeing closely with those obtained by direct measurement of the oxygen after thermal decomposition. However, the results only agreed provided that the H_2O_2 content of the liquid phase was not more than 20%. Results obtained by Kleve's method did not agree with those by the Pisarzhevskii or thermal decomposition methods.

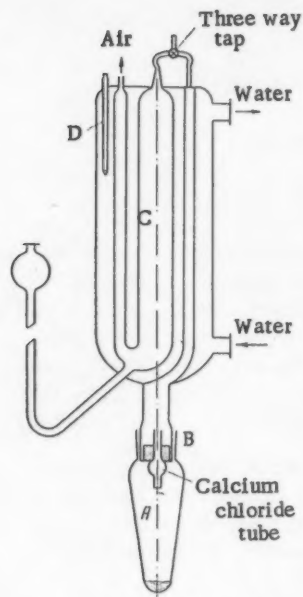


Fig. 1. Apparatus for the volumetric determination of active oxygen.

Formation of peroxy cerium compounds by interaction of $\text{Ce}(\text{OH})_4$ with hydrogen peroxide solution was relatively fast. Constancy of composition (for definite H_2O_2 concentration limits) of the solid phases, at 0 and -20° , was checked by periodic sampling and analysis. Table 1 shows some results for -20° , from which it appears that the composition of the solid phase CeO_3 had become stabilized after 2 hr.

When the data of Table 1 is applied to an $\text{H}_2\text{O}-\text{CeO}_2-\frac{1}{2}\text{O}_2$ triangular diagram, the points corresponding to all the residues lie on a straight line corresponding to the solid phase CeO_3 . All the results for the interaction of $\text{Ce}(\text{OH})_4$ with hydrogen peroxide solutions, at concentrations up to 96% in the liquid phase, obtained by the solubility method at 0 and -20° , are shown in Tables 2 and 3, and graphically in Figs. 2 and 3.

The above results establish quite definitely that within strictly determined H_2O_2 concentration limits, solid phases of the peroxide type are formed of overall composition $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$, CeO_3 , and $\text{CeO}_4 \cdot \text{CeO}_3 \cdot 2\text{H}_2\text{O}$ is the previously well known hydroperoxide type compound $\text{Ce}(\text{OOH})(\text{OH})_3$, and CeO_3 and CeO_4 are typical cerium peroxides. These cerium peroxy compounds formed at 0 and -20° can be fairly well separated from their mother liquors in the form of dry powders, orange to black in color. The residues corresponding to $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$ and CeO_3 decompose relatively quietly. The residue corresponding to CeO_4 is less stable and decomposes explosively. Because of this, when determining the active oxygen content of CeO_4 by the volumetric oxygen evolution method, it is necessary to cool instead of heating the sample tube.

TABLE 1. Data on the Time Required to Establish Equilibrium in the Reaction between $\text{Ce}(\text{OH})_4$ and H_2O_2 at -20°

Time, hr	Liquid phase composition %, w/w		Residue composition, % w/w		Solid phase
	O_2 active	H_2O_2	O_2 active	CeO_2	
1,0	12,20	25,93	8,48	72,10	CeO_3
1,5	12,26	26,06	8,75	72,33	CeO_3
2,0	12,19	25,90	8,13	75,53	CeO_3
3,0	12,30	26,15	8,03	70,75	CeO_3
4,0	12,28	26,14	8,28	76,44	CeO_3

Differential Heating Curves of Cerium Peroxy Compounds

The cerium peroxy compounds were investigated by differential thermal analysis, using a recording Kumakov pyrometer. The volume of oxygen evolved by thermal decomposition was recorded at the same time. As stated above, it was difficult to obtain these peroxy compounds quite dry and free from the hydrogen peroxide of the mother liquor. We therefore investigated solid phases containing an appreciable amount of highly concentrated hydrogen peroxide, and this affected their apparent behavior during thermal decomposition. If we attempted to apply normal preparative methods and to wash the products with alcohol and ether, their compositions changed significantly.

For instance, when such a treatment was applied to the "residue" corresponding to $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$, i.e., $\text{Ce}(\text{OOH})(\text{OH})_3$, and the material was then dried over P_2O_5 , the composition of the product corresponded quite closely to $\text{CeO}_3 \cdot \text{H}_2\text{O}$, i.e., $\text{O}=\text{Ce}(\text{OOH})(\text{OH})$, a compound not obtained in the study of the $\text{CeO}_2-\text{H}_2\text{O}-\frac{1}{2}\text{O}_2$ system at 0 and -20° . On the other hand, attempts to apply the same treatment to the more active CeO_4 inevitably led to formation of a hydrated product, of composition close to $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$.

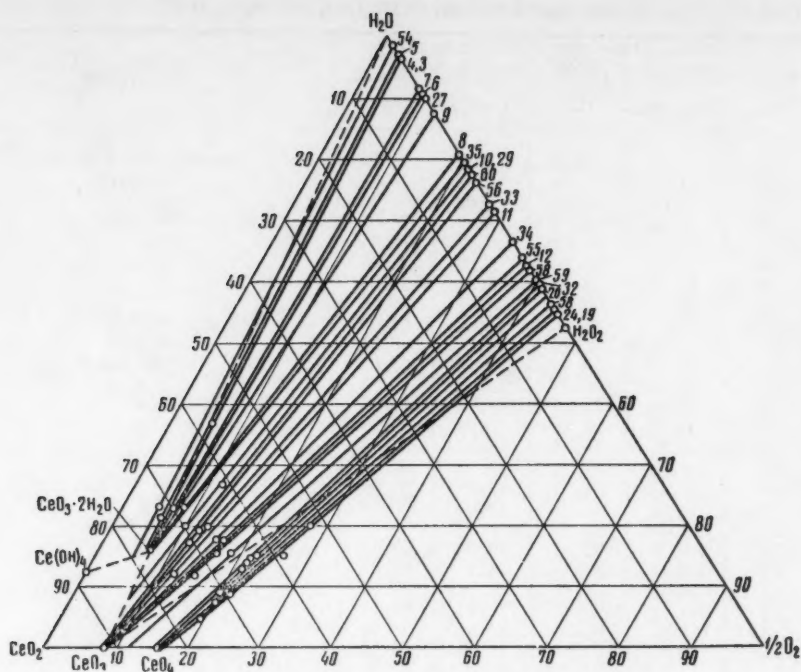


Fig. 2. Isotherms at 0° for the ternary system $\text{Ce}(\text{OH})_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$.

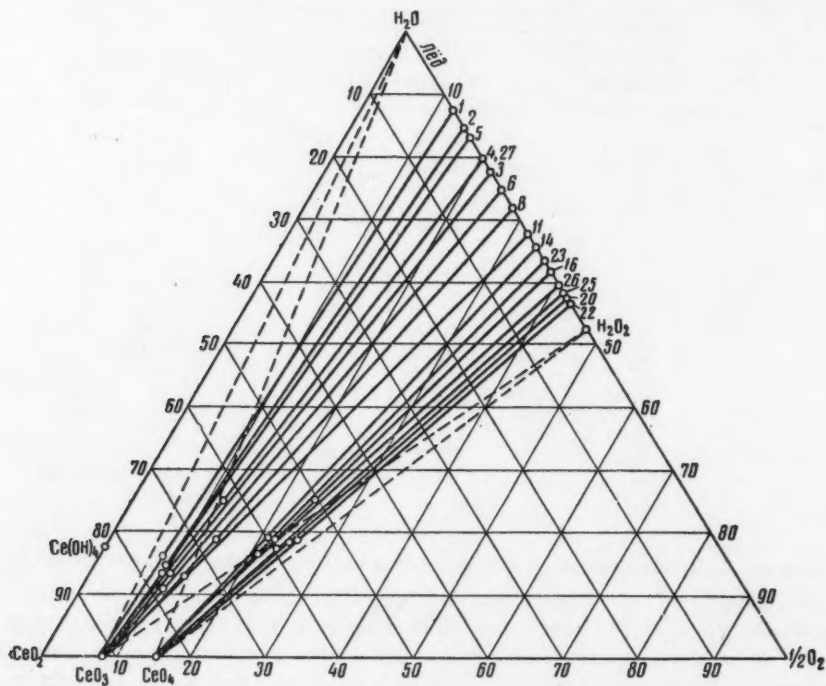


Fig. 3. Isotherms at -20° for the ternary system $\text{Ce}(\text{OH})_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$.

TABLE 2. Data for the Reaction between $\text{Ce}(\text{OH})_4$ and H_2O_2 at 0°

Expt. No.	Liquid phase composition, %, w/w		Residue composition, %, w/w		Solid phase
	O_2 active	H_2O_2	O_2 active	CeO_2	
54	1,52	3,23	4,79	71,96	$\text{Ce}(\text{OH})_4 + \text{CeO}_3 \cdot 2\text{H}_2\text{O}$
5	3,36	7,14	5,58	76,95	The same
4	3,69	7,80	6,06	69,78	$\text{CeO}_3 \cdot 2\text{H}_2\text{O}$
3	3,69	7,84	6,89	72,05	The same
7	8,96	19,04	6,67	70,94	"
6	9,07	19,28	5,91	73,27	"
9	12,53	26,66	8,59	74,52	"
8	19,13	40,67	8,47	68,16	"
10	21,38	45,40	12,62	61,09	$\text{CeO}_3 \cdot 2\text{H}_2\text{O} + \text{CeO}_3$
33	27,14	57,80	14,24	66,34	CeO_3
30	27,38	58,30	12,46	69,05	The same
11	28,83	61,29	12,74	75,37	"
34	33,66	71,66	15,14	66,85	"
55	36,76	78,15	16,99	67,95	"
57	36,85	78,34	15,71	66,48	"
58	37,78	80,32	15,70	66,32	"
59	39,77	84,55	18,88	65,50	$\text{CeO}_3 + \text{CeO}_4$
32	40,90	86,95	13,05	72,00	CeO_4
20	41,03	87,35	21,80	63,69	The same
58	43,76	93,03	20,30	70,34	"
42	43,13	91,69	21,18	65,10	"
44	44,41	94,41	19,37	75,80	"
40	44,72	95,07	20,12	69,43	"
43	44,81	95,26	21,52	68,70	"
15	45,10	95,88	21,29	69,53	"

TABLE 3. Data for the Reaction between $\text{Ce}(\text{OH})_4$ and H_2O_2 at -20°

Expt. No.	Liquid phase composition, %, w/w		Residue phase composition, %, w/w		Solid phase
	O_2 active	H_2O_2	O_2 active	CeO_2	
1	12,20	25,93	8,48	72,10	CeO_3
2	15,51	32,97	10,17	76,33	The same
5	16,86	35,84	9,75	76,26	"
27	20,37	43,30	12,75	62,88	"
4	20,58	43,98	10,95	75,97	"
3	22,63	48,11	11,26	78,48	"
6	25,39	53,98	11,64	78,00	"
8	28,33	60,23	14,58	66,75	"
11	32,54	69,18	13,05	74,23	"
14	34,41	73,15	21,36	60,06	CeO_4
23	36,65	77,95	21,70	57,60	The same
16	38,24	81,30	24,55	50,54	"
26	40,42	85,93	22,25	58,81	"
25	41,47	88,16	23,72	59,81	"
20	42,79	90,97	24,12	57,28	"
22	43,22	91,88	26,12	55,80	"
13	43,75	93,01	19,75	70,63	Freezes with formation of solid H_2O_2

Figures 4-6 show the differential thermal analysis curves and the oxygen evolution curves for "residues" corresponding to the solid phases $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$, CeO_3 , and CeO_4 . The differential curves are all similar in character with one exothermic effect at $10-20^\circ$ and one endothermic effect at $80-100^\circ$. However, the oxygen evolution curves vary considerably. With $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$ there is a continuous and relatively uniform oxygen evolution from the start, which trails off and ceases altogether after dehydration at 190° ; the product then has the approximate composition $\text{CeO}_2 \cdot 1.25\text{H}_2\text{O}$, contains no active oxygen, and may be considered as incompletely dehydrated $\text{Ce}(\text{OH})_4$. The oxygen evolution curve for CeO_3 is characterized by an abrupt jump, corresponding in time to the exothermic effect. Active oxygen evolution then corresponds to decomposition of hydrogen peroxide in the mother liquor up to 72° , and the over-all composition closely approximates to the formula $\text{CeO}_3 \cdot \text{H}_2\text{O}$. The second oxygen evolution stage is

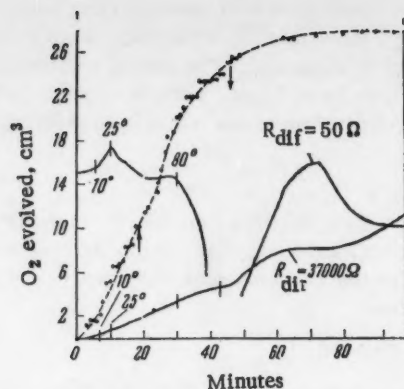


Fig. 4. Heating curves for the residue corresponding to $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$.

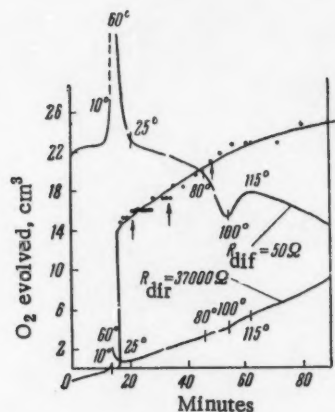


Fig. 6. Heating curves for the residue corresponding to CeO_4 .

TABLE 4. Dehydration Data for Cerium Peroxide

Time, days	Product composition, %, w/w		
	O_2 active	CeO_2	H_2O
0	7,03	—	—
1	5,37	36,30	63,33
2	7,12	47,15	45,73
4	8,54	81,60	9,96
6	8,83	81,32	9,85
$\text{CeO}_3 \cdot \text{H}_2\text{O}$	7,76	83,50	8,73

The same compound was obtained by adding a solution of ceric sulfate to a cold (0°) mixture of 150 ml of ammonia solution ($d = 0.994$) and 100 ml of 45% hydrogen peroxide. This gave an orange colored product containing active oxygen; it was dried in a desiccator over P_2O_5 at 0° . Table 4 gives some drying data.

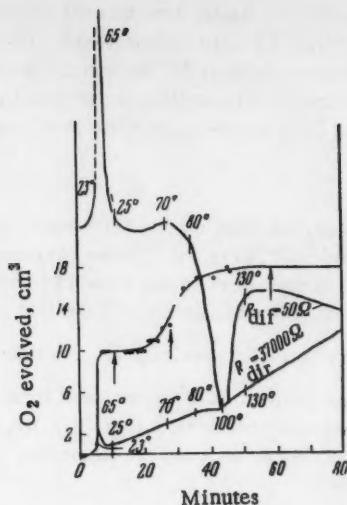


Fig. 5. Heating curves for the residue corresponding to CeO_3 .

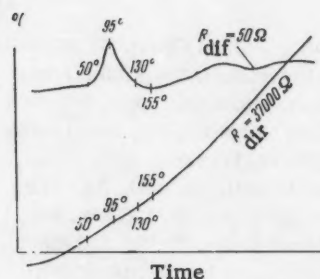


Fig. 7. Heating curve of $\text{CeO}_3 \cdot \text{H}_2\text{O}$.

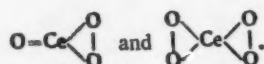
associated with decomposition of $\text{CeO}_3 \cdot \text{H}_2\text{O}$ to form more or less hydrated CeO_2 , which contains no active oxygen after the endothermic effect. At 215° the overall composition corresponds approximately to $\text{CeO}_2 \cdot \text{O} \cdot 7\text{H}_2\text{O}$. With the CeO_4 residue, as with CeO_3 , there is a vigorous oxygen evolution corresponding to the start of the exothermic effect. Further oxygen evolution is then gradual, and, at 150° , the partially dehydrated product contains no more than 1.7 H_2O per mole of CeO_2 .

These results show the important role of H_2O_2 adsorbed on cerium peroxy compounds, the relatively low stability of the damp residues, and their vigorous decomposition at relatively low temperatures. As stated above, the crude $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$ residue gave a product close to $\text{CeO}_3 \cdot \text{H}_2\text{O}$, after removal of excess absorbed H_2O_2 by washing with alcohol and ether and drying over P_2O_5 .

The analytical results show that the effect of drying was to give a product closely approximating in composition $\text{CeO}_3 \cdot \text{H}_2\text{O}$, i.e., the hydroperoxide $\text{O}=\text{Ce}(\text{OOH})(\text{OH})$. Figure 7 shows that this is thermally more stable; an exothermic effect begins at 50° , and an ill-defined endothermic effect at about 130° . The general character of the differential curve is characteristic for several hydroperoxides and for some perhydrates. There is reason to believe that CeO_3 and CeO_4 would be more stable if they could be freed adequately from excess of hydrogen peroxide.

SUMMARY

1. A study has been made of the reactions between $\text{Ce}(\text{OH})_4$ and H_2O_2 solutions up to 96.32% in the liquid phase, at 0 and -20° . The solid phases obtained were $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$, CeO_3 , and CeO_4 . Differential thermal analysis curves of the residues were characterized by an exothermic effect primarily associated with decomposition of absorbed hydrogen peroxide, and an endothermic effect due to dehydration.
2. Dehydration of the $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$ residue gave the compound $\text{CeO}_3 \cdot \text{H}_2\text{O}$.
3. Investigation of the properties of these cerium peroxy compounds indicated that $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{CeO}_3 \cdot \text{H}_2\text{O}$ were the hydroperoxy compounds $\text{Ce}(\text{OOH})(\text{OH})_2$ and $\text{CeO}(\text{OOH})(\text{OH})$. The compounds CeO_3 and CeO_4 are of the peroxide type and may be assigned the structures:



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PHYSICAL CHEMISTRY

INVESTIGATION INTO THE ADSORPTIVE PROPERTIES AND THE SECONDARY POROUS STRUCTURE OF ADSORBENTS ACTING AS MOLECULAR SIEVES

COMMUNICATION 2. COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES FOR THE MAXIMUM AMOUNTS AND VOLUMES ADSORBED BY SYNTHETIC ZEOLITES OF THE TYPE A

M. M. Dubinin

Institute of Physical Chemistry, Academy of Sciences of the USSR

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During the last ten years, in particular in England and in the United States, the synthesis and application of adsorbents of a new type, namely, porous aluminum silicate crystals belonging to the zeolite group, have been increasingly studied. These crystals gave a stable aluminum silicate frame and as a result of thermal dehydration, which is not accompanied by any noticeable change in the x-ray structure parameters of the skeleton, they acquire a porous structure. The occurrence of cavities with molecular dimensions, the entrances of which are formed by still narrower mouths or "windows," with sizes strictly fixed for each zeolite type, is characteristic for the porous structure of the zeolitic crystals. The synthetic zeolites are highly effective drying agents, and adsorbents with very pronounced selective properties; their selectivity originates from their particular adsorption kinetics, which are related to their molecular sieve action [1-8].

Two types of synthetic zeolites, type A, which has no analogy in nature [4] and type X, which is analogous to natural faujasite, have become of practical importance as industrial adsorbents. Each of them is used in the Na- or the Ca-form. By the hydrothermal synthesis one obtains microscopic zeolite crystals with sizes of a few tenths or several microns. For adsorption or adsorptive separation of vapors the synthetic zeolites are usually applied in the form of granules. The granules contain, besides highly dispersed zeolite crystals, also natural aluminum silicate used as a binding agent. The binder has practically no measurable adsorptive properties and plays the role of inert material.

In the present study we have attempted, starting from x-ray structure data of the literature and the chemical composition of the crystal unit cells in synthetic zeolites of type A, to calculate the maximum adsorption capacities and volumes for completely dehydrated crystals in the Na-form (NaA) and Ca-form (CaA), with the purpose of comparing them with the experimental results of adsorption measurements. An analogous analysis of adsorption characteristics for granulated zeolites will be reported in one of the next communications. Exhaustive data on the x-ray structure determination of type A zeolites are found in the papers [5, 6 and 8]. These data suffice to solve the problem raised.

According to the x-ray structure investigations, the aluminum silicate frame of the dehydrated type A zeolite is composed of identical cubooctahedral structural units containing 24 silicon and aluminum ions, which are connected with 36 oxygen ions.

In Fig. 1 the primitive cubical packing of the cubooctahedra in the zeolite A structure [7] is shown schematically. The silicon and aluminum ions are located at the corners of the cubooctahedra and the oxygen ions lie midway between the corners. The small cubes designate the four oxygen ions which serve as a bridge connecting the adjacent cubooctahedra.

A perspective drawing of this model [6] is given in Fig. 2. The space between the eight cubooctahedra constitutes the largest cavity in the zeolitic structure; its diameter is 11.4 Å and the octagonal windows, which have 4.2 ± 0.2 Å diameters and are formed by eight oxygen ions, are its entrances. The cavities inside the cubooctahedra

are the smaller cavities in the zeolite structure; they have 6.6 Å diameters and are bounded by hexagonal windows, which have 2-2.5 Å diameters and are formed by oxygen ions. The smallest cavities, with tetragonal windows, are inaccessible even to the smallest molecules [5]. In the Na-form eight of the 12 sodium ions are located in the centers of the hexagonal windows and the remaining four sodium ions are distributed statistically over the 12 possible positions in the cubical faces inside the smaller cavities [6].

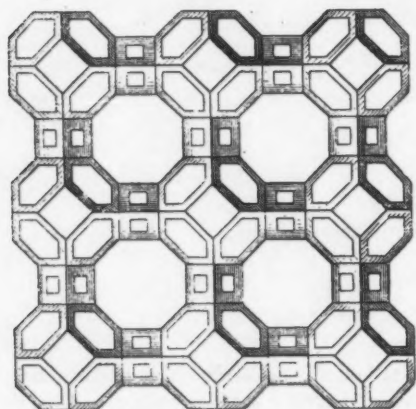


Fig. 1. Scheme showing how the cubooctahedra in the aluminum silicate frame of a type A zeolite are mutually arranged.

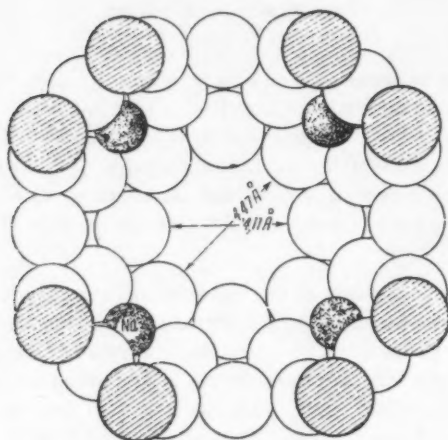


Fig. 3. Cross section of the largest cavity in the unit cell of a type NaA zeolite.



Fig. 2. Model of the aluminum silicate frame of a type A zeolite.

The center of the cubical unit cell in the zeolite crystal coincides with that of the largest cavity. Each unit cell has one largest cavity and eight smaller ones, which are located inside the cubooctahedra, where as their centers coincide with the corners of the cubical unit cell. In Fig. 3 a cross section through the center of the largest cavity in the unit cell of the NaA [8] zeolite is depicted. Oxygen ions are designated by open circles, but those cut by the plane of the cross section are marked as dashed circles. The small filled circles denote sodium ions. The silicon and aluminum ions are located in the tetrahedral voids between the oxygen ions and in Fig. 3 they are not shown. In the center of Fig. 3 the window formed by eight oxygen ions in the largest cavity is visible. By altogether six windows, each largest cavity is in communication with the adjacent ones and each of the latter, in its turn, is surrounded by six analogously located largest cavities, and so on. Since the centers of the largest cavity coincide with those of the unit cells, they form a cubical lattice. As is evident from the model shown in Fig. 2, the windows of the smaller cavities open into the largest one and precisely eight of them communicate to each largest cavities. The largest and the smaller cavities have a practically spherical shape.

By starting from the data on the composition of the unit cells of completely hydrated type A zeolites in their sodium and calcium forms, as are given in the papers [4, 5], and from the lattice parameters found in the same sources, we have calculated the main characteristics of the porous structure, the maximum adsorption capacity, the adsorption volume and some other properties of dehydrated zeolite crystals. The original data and the results of our calculations are assembled in Table 1.

TABLE 1. Basic Data on the Composition, Structure and Some Properties of Synthetic Type A Zeolites

	NaA	CaA
Unit cell (UC) composition	$\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 27\text{H}_2\text{O}$	$\text{Ca}_6[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]30\text{H}_2\text{O}$
Molecular weight of UC, M	2191	2209
Molecular weight of the aluminum silicate frame of the UC, M_c	1704	1669
Total molecular weight of the water of hydration, $M_{\text{H}_2\text{O}}$	486.4	540.5
UC mass, \underline{m}	$3.63 \cdot 10^{-21}$ g	$3.67 \cdot 10^{-22}$ g
UC parameter, a°	12.32 Å	12.26 Å
UC volume, V_u	1870 Å ³	4183 Å ³
X-ray density of the hydrated zeolite, d_x	1.945 g/cm ³	1.990 g/cm ³
Apparent x-ray density of the hydrated zeolite, δ_x	1.513 g/cm ³	1.503 g/cm ³
Experimental density of the hydrated zeolite, \underline{d}	1.990 ± 0.004 g/cm ³	2.05 g/cm ³
Apparent density of the hydrated zeolite calculated from \underline{d} , δ	1.548 g/cm ³	1.548 g/cm ³
Ratio \underline{d}/δ_x	1.023	1.030
H ₂ O content in the hydrated zeolite, as is found from UC composition, N	22.20%	24.47%
H ₂ O content when referred to a unit mass of dehydrated zeolite, a_0	0.285 g/g; 15.84 mM/g	0.324 g/g; 17.97 mM/g
Calculated maximum of the H ₂ O volume adsorbed when it is expressed as liquid of the normal density at 20°, V_0	0.286 cm ³ /g	0.325 cm ³ /g
Volume of the UC cavities as is found from V_0 , V_p	803 Å ³	900 Å ³
Porosity of the dehydrated zeolite crystal, P	43.0%	48.7%
Apparent diameter of the windows in the greater cavities as is found from the experimental data, d^0	4.2-4.75 Å	5.0-5.6 Å

From the composition of the unit crystal cells for completely hydrated type A zeolites in their sodium and calcium forms we have calculated the following molecular weights: M , that of the unit cell, M_c , that of its aluminum silicate frame and $M_{\text{H}_2\text{O}}$, that of the total amount of hydration water, which fills the cavities in the unit cells of the zeolite crystals. By multiplying the molecular weight M of the unit cell by the mass m_0 of the atomic weights unit we get the following expression for the actual weight \underline{m} of the unit cell in the hydrated zeolite

$$\underline{m} = m_0 M, \quad (1)$$

where $m_0 = 1.66 \cdot 10^{-24}$ g.

From the lattice parameters \underline{a} of the cubical crystals we have calculated the volumes V_u of the unit cells

$$V_u = \underline{a}^3 \quad (2)$$

Upon dividing the mass of the unit cell by its volume we found the x-ray density d_X of the hydrated zeolite crystal

$$d_X = m/V_u \quad (3)$$

By calculating in an analogous way the mass m_c of the aluminum silicate frame of the unit cell we got the apparent x-ray density δ_X of the dehydrated zeolite, under the assumption that dehydration does not change the volume of the unit cell. Actually, according to Barrer's experiments [6], the unit cell volume of the hydrated zeolite is 8 \AA^3 or 0.43% greater than that of the dehydrated crystals. In our calculations this change may be neglected, so that

$$\delta_X = m_c/V_u \quad (4)$$

The experimental values of the actual densities \underline{d} in hydrated zeolite crystals are given in Table 1; on the average they are 2.5% greater than the x-ray densities. The water content in completely hydrated zeolite crystals may be easily calculated from the total molecular weight M_{H_2O} of the water molecules filling the cavities of the unit cell and from the molecular weight M of the unit cell itself

$$N = M_{H_2O} \cdot 100/M \% \quad (5)$$

Since the zeolite CaA has a higher water content and a smaller molecular weight of the unit cell, the value of N for the Ca-form is about 10% higher than that for the Na-form. As we know the water content of hydrated zeolites, the apparent density δ of the dehydrated crystals can be easily derived from the experimental values of the actual density \underline{d}

$$\delta = d(1 - 0.01N) \quad (6)$$

From the molecular weights M_{H_2O} and M_c it is easy to calculate the maximum amount of water vapor a_0 which can be adsorbed per unit mass of dehydrated zeolite, if it is assumed that the hydration and dehydration are completely reversible

$$a_0 = M_{H_2O}/M_c \text{ g/g} \quad (7)$$

or

$$a_0 = M_{H_2O} 1000/M_c 18.02 \text{ mm/g} \quad (8)$$

When taking the normal density of water at 20° , 0.998 g/cm^3 , this maximum capacity is equal to the volume adsorbed

$$V_0 = a_0/0.998 \text{ cm}^3/\text{g} \quad (9)$$

According to the data of Table 1, the maximum amounts and volumes adsorbed are quite different for the zeolite crystals NaA and CaA. From the maximum volume of water adsorbed V_0 the cavity volume in the unit cell of the dehydrated zeolite can be easily estimated. For this one must know the number of unit cells per unit mass of dehydrated zeolite crystal. It is evident that

$$n = 1/M_c m_0 \text{ g}^{-1} \quad (10)$$

where M_c is the molecular weight of the unit cell of the dehydrated zeolite and m_0 the mass of the atomic weight unit.

From the calculated value for the maximum volume of water adsorbed V_0 the cavity volume per unit mass of dehydrated zeolite V'_p is expressed by

$$V'_p = V_0/n \quad (11)$$

According to the data of Table 1 the cavity volumes in the unit cells of the zeolites NaA and CaA differ by about 12%.

From the cavity volumes V'_p of the zeolite unit cells and the volumes V_u of the unit volumes themselves it is easy to estimate the porosity P of the dehydrated zeolite crystals

$$P = V'_p 100/V_u \% \quad (12)$$

According to the data of Table 1 the porosity of the dehydrated CaA crystals differs considerably from that of NaA.

In the last line of Table 1 we give the apparent diameters d^0 of the windows in the largest zeolite cavities, as were estimated from the critical sizes of those molecules which are able to pass through the windows into the cavities [4], that is, are adsorbed.

TABLE 2. Porous Structure of Dehydrated CaA Zeolite Crystals

Unit cell (UC) parameter of the crystal, a^0	12,26 Å
UC volume, V_u	1843 Å ³
Diameter of the greater UC cavity, d_δ	11,4 Å
Diameter of the smaller UC cavity, d_M	6,6 Å
Volume of the greater UC cavity, V_δ	776 Å ³
Volume of the smaller UC cavity, V_M	150 Å ³
Total UC cavity volume, V_P	926 Å ³
Fraction of the volume of the greater cavities in the total UC cavity volume, α	0,838
Porosity of the zeolite crystals, P	50,2%
Theoretical value for the maximum volume adsorbed by the zeolite crystals, V	0,334 cm ³ /g
Theoretical value for the volume adsorbed in the greater cavities of the zeolite crystals, V'	0,280 cm ³ /g
Maximum value of H ₂ O adsorbed when calculated as liquid with the normal density at 20°, V_0	0,325 cm ³ /g
Total UC cavity volume found from V_0 , V_P'	900 Å ³

For the zeolite CaA, as an example, in Table 2 there is given more detailed information on the porous structure of dehydrated crystals. Some structural parameters inserted into Table 2 have already been noted in Table 1. The volumes of the largest and the smaller cavities were calculated as the volumes of the spheres described by their diameters. As has already been noted above, each unit cell of the zeolite corresponds to one largest and one smaller cavity. Therefore, the total volume V_P of the cavities in the unit cell of the dehydrated zeolite is found by adding the volume V_δ of the largest cavity to that V_M of the smaller one.

$$V_P = V_\delta + V_M \quad (13)$$

The fraction α of the largest cavity volume in the total cavity volume

$$\alpha = V_\delta / V_P \quad (14)$$

amounts to 0,838.

The theoretical value of the porosity in dehydrated CaA zeolite crystals equals 50,2%.

$$P = V_P / V_u \cdot 100 \% \quad (15)$$

From the theoretically estimated value of the cavity volume V_P in the unit cell, one can calculate the pore volume per unit mass of dehydrated zeolite, that is, the theoretical value of the maximum adsorption capacity for such molecules as for instance those of water, which are able to penetrate into both the largest and the smaller cavities

$$V = V_P / M_C m_0 \quad (16)$$

where M_C is the molecular weight of the aluminum silicate frame of the unit cell. The calculated value $V = 0,334$ cm³/g differs only slightly from the maximum volume of water adsorbed $V_0 = 0,325$ cm³/g, as is found from the composition of the unit cell when the normal liquid density at 20° is used.

The fact that the volumes V and V_0 are nearly equal proves that the packing of water molecules in the cavities of the hydrated zeolite CaA scarcely differs from that in the liquid. Unlike the oxygen atoms (ions) of the aluminum silicate frame, the oxygen atoms of the water molecules could not be found in the x-ray determination

TABLE 3. Comparison of the Calculated and Experimental Values for the Maximum Amounts and Volumes Adsorbed by Synthetic Type A Zeolite Crystals

Zeolite form	Zeolite samples	H ₂ O, 20°			N ₂ , -195°		
		p/p _s	a ₀ , mM/g	V ₀ , cm ³ /g	p/p _s	a ₀ , mM/g	V ₀ , cm ³ /g
NaA	Values calculated from the composition of unit cell		15.84	0.285			
	4A Linde, Breck's experiments*	1.0	16.0	0.289			
	4A Linde, Barrer's experiments**	0.80	16.0	0.289			
	4A Linde, Our experiments***	0.85	12.2	0.218			
	Mirskii No. 275	0.9	15.5	0.280			
	Maksimovaya No. 90	0.85	15.0	0.270			
	Maksimovaya 1 exp. sample	0.9	16.3	0.294			
	Neimark No. 300	0.9	13.6	0.245			
	Lipkind No. 202-2	0.9	15.2	0.273			
CaA	Values calculated from the composition of unit cell		17.97	0.325			
	Theoretical value from x-ray structure data			0.334			0.280
	5A Linde, Breck's experiments*	1.0	16.85	0.305	0.92	8.53	0.296
	5A Linde, Our experiments***	0.90	12.3	0.222	0.85	6.22	0.216
	Mirskii No. 276	0.90	17.4	0.314	0.90	8.20	0.284

* In the study by Breck and others the a₀ values [4] were determined at p/p_s = 1 and, therefore, they may be somewhat too high.

** Calculated from Barrer's data [6] on the water content in the zeolite NaA, when it is in equilibrium with the water vapor over a saturated solution of ammonium chloride.

*** The industrial samples of the crystalline zeolites 4A and 5A from Linde which were at our disposal showed markedly lowered adsorptive properties with respect to water vapor (see, for instance, Fig. 4). In our experiment, for all zeolite samples the a₀ values were obtained from the experimental isotherms determined by means of a sorption balance. Dehydration of the zeolites was carried out at 350° during six hours under evacuation to a residual pressure equal to ~1 · 10⁻⁶ mm Hg.

of the hydrated zeolite structure, and this indicates that the state of water in the hydrated zeolite is similar to that in the liquid. Consequently, the water molecules do not occupy fixed positions in the zeolite cavities.

As has already been noted, both the largest and the smaller cavities of the dehydrated crystals are accessible to water molecules. However, since in the zeolite NaA the sodium ions are located in the centers of the hexagonal windows of the smaller cavities, penetration of water molecules into the smaller cavities is coupled with displacement of sodium ions from their positions in the centers of the smaller cavity windows with a diameter 2-2.5 Å [4].

Bigger molecules, for instance those of nitrogen, cannot pass through the windows of the smaller cavities. Obviously, the theoretical value of the maximum volume adsorbed for such substances corresponds to filling of only the volume of the largest cavities, that is, it will be the fraction α of the total cavity volume V in the dehydrated

zeolite crystal. In the case considered the theoretical value of the maximum volume adsorbed will amount to

$$V' = \alpha V \quad (17)$$

For the dehydrated zeolite CaA this volume $V' = 0,280 \text{ cm}^3/\text{g}$. If the maximum volume adsorbed is estimated from that for water, where $V_0 = 0,325 \text{ cm}^3/\text{g}$, then one gets $V'_0 = \alpha V_0 = 0,272 \text{ cm}^3/\text{g}$. The difference between V' and V'_0 is trifling.

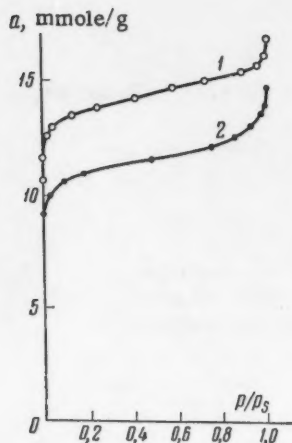


Fig. 4. Sorption isotherm of water vapor at 20° on dehydrated zeolite crystals of the type NaA: 1) L. M. Maksimovaya's sample No. 90; 2) sample of Linde 4A (USA).

At present we are able to compare the theoretical and experimental values of the maximum amounts and volumes adsorbed on American and Soviet samples of synthetic crystalline zeolites. This is most expediently done by comparing the adsorptive properties of the zeolites with respect to at least two vapors, with such molecules that both the largest and the smaller cavities are accessible to one of the vapors and only the largest cavities are accessible to the other. Water may serve as an example of the first kind of vapor and nitrogen at a sufficiently low temperature, for instance at its boiling point (-195°), may serve as one of the second kind. It should be noted that under these conditions, nitrogen is quite rapidly adsorbed only on the CaA zeolite; its adsorption rate on the NaA zeolite is immeasurably small, since the penetration of the nitrogen molecules via the windows of the largest cavities is characterized by a considerable energy of activation. At the higher temperature of -78° nitrogen is slowly sorbed by the NaA zeolite. However, the equilibrium is, for practical purposes, not attained [9].

Usually, the synthetic zeolite crystals have sizes of the order of microns and the samples which we used may be considered to constitute a heap of contacting particles. Therefore, at high relative pressures the adsorption process is complicated by capillary condensation in the spaces between the contacting, highly dispersed crystals.

As an example, sorption isotherms of water vapor at 20° on samples of powders of the crystalline type NaA zeolite are shown in Fig. 4. The adsorption branches of the curves rise smoothly in the region of intermediate relative pressures, but bend steeply upwards at relative pressures close to one, as a result of capillary condensation of water vapor in the spaces between the contacting particles. Therefore, the maximum adsorption capacity and the corresponding maximum volume adsorbed V_s cannot serve as characteristics of the maximum volume adsorbed by the porous dehydrated zeolite crystals. The most rational choice is to estimate the latter volume from the amount adsorbed at the point where the final bend of the isotherm in the high relative pressure region starts, that is, at $p/p_s = 0.85-0.90$. In this way the maximum mm/g were amounts adsorbed a_0 determined from the experimental isotherms. When calculating the maximum volume adsorbed per unit mass of the original dehydrated zeolite $V_0 \text{ cm}^3/\text{g}$, we used the normal densities of water at 20° and nitrogen at -195° , that is, we took the values corresponding to the liquid phases.

In Table 3 the experimentally determined values of the maximum amounts and volumes adsorbed for American and Soviet samples of synthetic type A zeolites are compared with the estimated theoretical values.

According to the data of Table 3, the experimental values of the maximum amounts and volumes adsorbed in the case of water and nitrogen, both for the Soviet and the American samples of synthetic type A zeolites, coincide with the estimated theoretical ones. Consequently, only by dehydration do the zeolite crystals acquire a porous structure; the completely hydrated zeolites are nonporous solids. Porous crystals and, in particular, type A zeolites are of great interest for adsorption studies, since they are porous adsorbents for which the volume, sizes and shape of the pores and the nature of the surface too are known from independent measurements.

The adsorption measurements were carried out by E. D. Zaverina and E. G. Zhukovskaya. The author feels himself obliged to thank B. A. Lipkind, L. M. Maksimovaya, Ya. V. Mirskii and I. E. Neimark for giving their synthesized zeolite samples for his investigation.

SUMMARY

By starting from data of the literature on the x-ray structure determinations and the composition of the unit cells in crystals of type A zeolites we have calculated limiting values for the amounts and volumes adsorbed by the said zeolites, and these values are in good agreement with the experimental data.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

SORPTION KINETICS OF WATER VAPOR ON TYPE A ZEOLITES

D. P. Timofeev and I. T. Erashko

Institute of Physical Chemistry, Academy of Sciences of the USSR

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For some time past, synthetic zeolites have found an ever wider application in drying and separation of gaseous and liquid mixtures. These new narrow-porous sorbents, called "molecular sieves," have highly selective properties and differ from natural zeolites by possessing a more symmetrical and homogeneous pore structure. The latter fact, together with the great practical importance of the synthetic zeolites, makes them very interesting objects for an investigation. In spite of the rather great number of studies devoted to investigation of the adsorptive properties of the zeolites (a review of the main papers is given in Barrer's article [1]), the sorption kinetics of water vapor on zeolites has been clarified very little. The previous investigations were done with natural zeolites [2-4], so we thought it expedient to undertake a study of a synthetic one. In the present paper are given the results obtained upon investigating the sorption kinetics of water vapor in the region of high coverages on a granulated Linde 5A molecular sieve with 1.6 mm granule radius.

EXPERIMENTAL

1. The sorption kinetics were measured at a constant water vapor pressure under vacuum conditions by means of a sorption balance. We do not give the scheme of the set-up, since it hardly differs from the balance equipment usually applied for measuring the sorption isotherm, and only an additional container of about 10 liter connected to the apparatus was included so that during the experiment the pressure of water vapor did not change very much. At pressures below 1 mm Hg (some tenths of a millimeter) an ampoule with water kept at the required temperature was connected to the apparatus in order to maintain a constant vapor pressure.

By carefully cutting away the edges, the sorbent granules used for the experiments were transformed into cylinders (with flat bases) with a length equal to the diameter; this was done to facilitate the calculation of the diffusion constant. The sorbent sample, consisting of several granules, was placed on the balance cup and evacuated by means of a mercury pump during 3-4 hr at a temperature of 350°. Then the connection between the sorption tube and the rest of the apparatus was broken and the required pressure of water vapor was established in the system. This pressure somewhat exceeded that of the operation conditions, since the subsequent volume increase and the corresponding lowering of the pressure, as results from reestablishing the connection with the sorption tube, was taken into account. After this the sorbent was brought to the temperature of the experiment in a water thermostat, and the stopcock which connects the sorption tube to the apparatus was opened. No measurements were done at the first admission of water vapor and the sorbent was only saturated to equilibrium. Later on, all operations of water admission were repeated, a higher vapor pressure was established and the measurements were started. The increments of the amount adsorbed were determined from the elongation of the helix of the sorption balance by means of a cathetometer with 0.01 mm scale divisions. The sensitivity of the helix was $2.44 \cdot 10^{-3}$ g/mm. The experiments were done at the temperatures 0 and 30°, while in the first case the temperature of the air thermostat in which the apparatus was mounted was kept at 20° and in the second case at 30°.

The diffusion coefficients were calculated from the diffusion equation for a cylinder with finite dimensions

$$\gamma = \frac{a}{a_{\infty}} = 1 - \frac{32}{\pi^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{\mu_n^2 (2m-1)^2} \exp \left[- \left(\frac{\mu_n^2}{R^2} + \frac{(2m-1)^2 \pi^2}{L^2} \right) D t \right] \quad (1)$$

where γ represents the relative amount adsorbed; a the amount adsorbed at the instant t ; a_{∞} the amount adsorbed at equilibrium ($t \rightarrow \infty$); μ_n the n th root of the Bessel function J_0 ; D the diffusion constant; R and L the radius and the length of the cylinder, respectively; $n = 1, 2, 3, \dots$ and $m = 1, 2, 3, \dots$. For the calculation of D equation (1) may be

modified and reduced to a more handy form. If one takes $\gamma = 0.5$ and designates the time required to attain this amount adsorbed by $t_{0.5}$, then from Eq. (1) one gets easily the following relation, which is convenient for calculation

$$D = k \frac{R^2}{\pi^2 t_{0.5}} \quad (2)$$

where k is a coefficient which depends on the ratio between the length and the radius of the cylinder. For a cylinder with a length equal to its radius, as was used in our experiments, $k = 0.318$ [5], that is

$$D = 0.318 \frac{R^2}{\pi^2 t_{0.5}} \quad (3)$$

Equation (1) is valid when $D = \text{const}$, which generally may not be the case. Therefore, the diffusion coefficients were measured in relatively narrow ranges of the amount adsorbed. In this case Eq. (1) stays valid, but

$$\gamma = \frac{a - a_1}{a_{\infty} - a_1} \quad (4)$$

where a_1 represents the equilibrium amount adsorbed at the start of the experiment at $t = 0$.

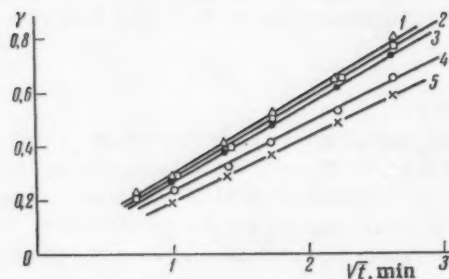


Fig. 1. The experimental data plotted in the coordinates γ versus \sqrt{t} , $t^\circ = 0^\circ$: 1) mean amount adsorbed $\bar{a} = 11.88$ mM/g; 2) $\bar{a} = 11.25$ mM/g; 3) $\bar{a} = 12.66$ mM/g; 4) $\bar{a} = 13.42$ mM/g; 5) $\bar{a} = 10.71$ mM/g.

2. In Fig. 1 the experimental results obtained at the temperature 0° are plotted in the coordinates γ versus \sqrt{t} . Up to the relative amount adsorbed $\gamma = 0.6-0.7$ the experimental points lie quite well on straight lines. Analogous results were obtained in the experiments at 30° , although in this case the straight lines do not pass through the origin but have a certain intercept with the ordinate axis. From the plots obtained we found the values of $t_{0.5}$ and calculated the diffusion constants by means of relation (2). In the range of coverages studied the diffusion constant in a complicated way depends on the amount adsorbed: at first it rises, goes through a maximum and then drops. The way in which the diffusion coefficient depends on the amount adsorbed is given by the curves shown in Fig. 2. The experimental points deviate somewhat, because the reproducibility of the experimental results is not very good. As is evident from the said figure, the diffusion constants at the temperature 30° exceed by a few times the values obtained at 0° and this indicates that the diffusion has the character of an activated process.

The coefficient of an activated diffusion depends upon temperature in the way expressed by the equation

$$D = D_0 e^{-\frac{E}{RT}}, \quad (5)$$

Where E is the activation energy; D_0 the preexponential factor; R the gas constant; T the temperature. From the D values determined at two temperature one may find the activation energy of the diffusional process by using the relation

$$E = 4.57 \frac{T_1 T_2}{T_2 - T_1} \lg \frac{D_2}{D_1}, \quad (6)$$

where D_1 and D_2 are the diffusion constants corresponding to the temperatures T_1 and T_2 , respectively.

The activation energies, as were calculated by means of relation (6) for various amounts adsorbed, are given in Table 1. From the data of Table 1 it is evident that the activation energy falls at increasing amounts adsorbed. The isosteric heats of adsorption which were calculated from the water vapor isotherms at 0 and 30° decrease from 11 to 10 kcal/mole in the range of coverages studied.

DISCUSSION

A framework consisting of SiO_4 and AlO_4 tetrahedra and having a unit cell as is schematically shown in Fig. 3 [1] makes up the structure of the zeolites. Inside the unit cell there is a spherical cavity with a radius of 11.8 Å and this cavity constitutes the main volume into which the molecules are sorbed. By six octagonal windows the sorptive volume of the cavity is connected to other identical cells. The diffusion of the gas molecules inside the crystal takes place via these windows. An aluminum atom possesses fewer valence electrons than a silicon atom and the resulting negative charge of the AlO_4 tetrahedron is compensated by calcium ions in the molecular sieve 5A or by sodium ions in the molecular sieve 4A.

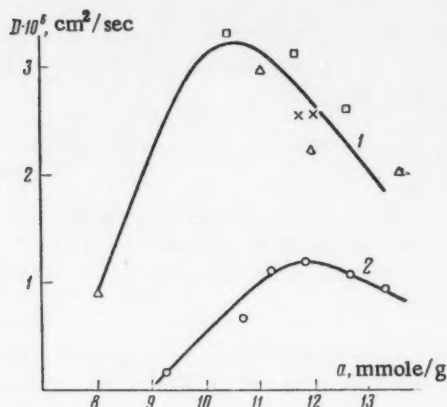


Fig. 2. The diffusion constant plotted versus the amount adsorbed; 1) $t^* = 30^\circ$; (Δ , \square) designate repeated experiments with one and the same sorbent portion; (\times) experiments with another portion; 2) $t^* = 0^\circ$.

TABLE 1. The Activation Energy as a Function of the Amount of Water Vapor Adsorbed on the Zeolite 5A ($0-30^\circ$)

a, mmole/g	E, cal/mole
11	6600
12	4800
13	4600

Since ion-dipole interaction is the essential energetic reason why the polar water molecules are sorbed by the zeolites, they are grouped first of all around the cations. According to data of the x-ray structure determinations by Taylor [6, 7], the sodium ion in the crystal lattice of zeolites is surrounded by two water molecules; the situation around a calcium ion is less fixed, in some structures it is surrounded by three water molecules. In the unit cell of the synthetic zeolite 5A there are six calcium ions, if the replacement of sodium by calcium ions is complete. In the paper [8] there is reported a chemical composition of a type 5A zeolite having four calcium and four sodium atoms in its unit cell. Both in the latter and in the former

case one finds, if one starts from the values given by Taylor for the number of water molecules per cation, that the first layer of the "water shell" which covers the surface of the spherical cavity contains about 18-20 water molecules, which amounts to 19-20% of the total weight of the unit cell. Our experiments were done in the range of coverages equal to 18-24% of the sorbent weight, that is, in the region where water vapor adsorption takes place in the remaining part of the sorptive volume in the cell.

The diameter of that part of the cavity which remains unoccupied, after the most active sites near the cations have been filled, is approximately equal to the difference between the diameter of the sphere inscribed in the cell and two times the diameter of a water molecule. If the latter is taken to be 2 Å (the sum of the internuclear distances and the covalent radii), then the diameter of the unoccupied part of the cavity is found to be 7.8 Å. Therefore, the longest path of a molecule inside the cell at the transition to an activated state is equal to 5.8 Å. When it is moving in other directions inside the boundaries of a cell, this distance is much smaller and under these conditions it is impossible to distinguish between diffusion along the surface and in the gas phase. When a molecule passes from one cell to another one, the length of its path increases correspondingly. The mean value of an elementary displacement may be calculated from the relation

$$D_0 = \frac{\Delta^2}{c} \nu, \quad (7)$$

where $\nu \approx 10^{13} \text{ sec}^{-1}$ is the vibration frequency of atoms in the lattice; c a constant which is dependent on the number of possible displacements. The numerical value of D_0 is found from Eq. (5). Before we derive this value, first we specify more accurately the physical sense and the magnitude of the diffusion constant D . The zeolite granules constitute an assembly of a great number of highly dispersed crystals, the sizes of which vary between some

tenths of a micron and a few microns. The voids between the contacting crystals form the secondary porosity [9] and they have about the same dimensions as the crystals. In Fig. 4 the differential curve for the distribution of the secondary pore volume in the sample studied is given as a function of the logarithm of the effective radius. The main part of the volume is due to pores with radii between 400 and 4000 Å. The most frequent pore radius is 2500 Å.

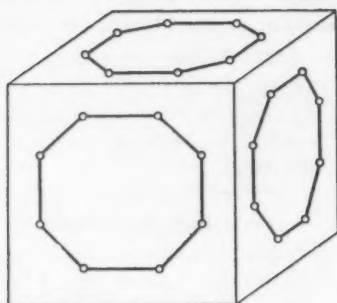


Fig. 3. Diagram showing the cell of the anion frame in a type A zeolite (the circles designate silicon and aluminum atoms; oxygen atoms are not indicated).

TABLE 2. D_0 and Δ Values at Various Coverages

a, mM/g	D_0 , cm ² /sec	Δ , Å	
		c = 4	c = 6
11	$14.0 \cdot 10^{-3}$	7.5	9.2
12	$5.5 \cdot 10^{-3}$	4.7	5.7
13	$2.8 \cdot 10^{-3}$	3.3	4.1

the ratio of the free path inside the crystal to the total free path of the diffusing molecules. In the intercrystalline voids diffusion can take place via the gas phase and along the outer surface of the crystals. The experiments were carried out at pressures not surpassing 26 mm Hg, so that under these conditions the free path of the molecules ($10^{-3} - 10^{-4}$) was longer than the dimensions of the intercrystalline voids and, consequently, the transfer in the gas phase was brought about by Knudsen diffusion. The diffusion coefficient for an infinitely long capillary is given by the equation

$$D_K = \frac{2}{3} \bar{u} r, \quad (9)$$

where \bar{u} is the kinetic velocity of the molecules (for water at 20° $\bar{u} = 5.1 \cdot 10^4$ cm/sec); r the radius of the capillary.

By substituting into formula (9) the value of \bar{u} and r (2500 Å) we get $D \approx 1$ cm²/sec. If a correction as given by Clausius [10] is applied for the finiteness of the length of the capillary, then the value of the coefficient is lowered to 0.4 cm²/sec. In the range of coverages studied the Henry constant H amounted to 2000-5000 and, consequently, the effective coefficient of diffusion via the gas phase was equal to $D_e = D_K/H = 0.8 \cdot 10^{-4}$ to $2 \cdot 10^{-4}$ cm²/sec, that is, two orders of magnitude higher than the values found experimentally. Hence it follows that diffusion inside the zeolite crystals gives the main diffusional resistance. An estimate of molecular migration along the outer surface of the crystals may just serve as an additional argument to strengthen the conclusion drawn. If we therefore, take that $D_{II} \ll D_I$, we find from relation (8) that

$$D = \frac{D_{II}}{\alpha} \quad (10)$$

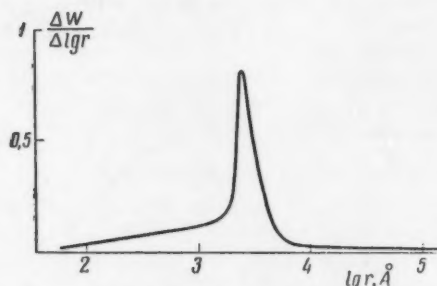


Fig. 4. Distribution of the secondary pore volume in the studied zeolite 5A when plotted as a function of the logarithm of the effective radius.

In the zeolite granules the diffusion takes place via the intercrystalline voids and inside the crystals. In such a bidisperse (with respect to pore sizes) medium the overall diffusion coefficient may be expressed by the relation

$$D = \frac{D_I D_{II}}{D_{II} (1 - \alpha) + \alpha D_I}, \quad (8)$$

where D_I is the diffusion coefficient in the intercrystalline space; D_{II} the diffusion coefficient inside the crystal; α

that is, the coefficient of internal diffusion, as it is determined in the experiment, is greater than the diffusion coefficient in the crystals, since $\alpha < 1$. For a homogeneous structure as exists in the synthetic zeolites the magnitude of $(1 - \alpha)$ is numerically equal to the secondary porosity ϵ_2 when expressed in cm^3/cm^3 , and Eq. (10) may be rewritten in the following way

$$D = \frac{D_{II}}{1 - \epsilon_2} \quad (11)$$

The secondary pore volume of the sample studied amounted to $0.335 \text{ cm}^3/\text{g}$; the apparent specific weight of the granules after dehydration was $1.1 \text{ g}/\text{cm}^3$ and, consequently, $\epsilon_2 = 0.37 \text{ cm}^3/\text{cm}^3$. When this value is substituted into (11), it turns out that the diffusion coefficients in the crystals are 1.59 times smaller than the values found from the experiment. The values of D_0 which were calculated for various coverages by using Eq. (5) and taking into account relation (11) are assembled in Table 2.

In Table 2 are also given the path lengths Δ at the transition of the molecule into the activated state. From the data in Table 2 it follows that Δ and, correspondingly, D_0 decrease when the adsorptive volume is occupied to a higher extent. In this case the decrease of D_0 has a stronger influence on the diffusion coefficient than does the change in the factor $e^{-E/RT}$; the diffusion coefficient drops, although the activation energy too decreases. The Δ values found are in satisfactory agreement with the molecular path lengths at the elementary displacements in the sorption cell, as are found from purely geometrical considerations.

SUMMARY

1. The sorption kinetics of water vapor on the granulated molecular sieve Linde 5A have been studied in the region of high coverages at the temperatures 0 and 30° . It has been found that the diffusion coefficients change with the amount adsorbed and attain a maximum near the amount adsorbed 11-12 mm/g.

2. The mechanism of water vapor transfer in granulated zeolites has been discussed and an approximate formula relating the diffusion coefficient in the granules to that in the zeolite crystals has been proposed.

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THE COMPENSATION EFFECT IN ACTIVATION PROCESSES
FROM THE POINT OF VIEW OF STATISTICAL KINETICS
PART 2. POSSIBLE PHYSICAL CAUSES FOR THE APPEARANCE OF THE
COMPENSATION EFFECT IN CERTAIN SYSTEMS AND PROCESSES

S. Z. Roginskii and Yu. L. Khaif

Institute of Physical Chemistry, Academy of Sciences of the USSR

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In the previous communication [1], and also in [2] it has been shown by use of the method of calculating the rates of activation processes [3], that it is possible to obtain formulas for the rates of activation processes without additional assumptions in which the relationship between the preexponential factor and the activation energy is expressed. The following formula has been obtained for the probability W (in relation to unit time) of the elementary act of the activation process of a definite type within the volume l^3 :

$$W = q \frac{kT}{\hbar} \exp \left\{ \frac{E^2}{2\alpha^2} \right\} \exp \left\{ -\frac{E}{kT} \right\}, \quad (1)$$

where the quantity l is limited by the conditions [3]

$$l^3 \leq \frac{Ed^3}{\gamma \hbar v}; \quad l^3 \gg \frac{E}{\gamma kT} d^3, \quad (2)$$

where γ = number of degrees of freedom of given type in the volume d^3 ; v = mean rate of energy transfer by the quasi-particles (particles playing a basic role in processes of the type considered); k = the Boltzmann constant; T = absolute temperature; and α^2 = dispersion of the energy distribution in the degrees of freedom considered within the region l^3 , determined by the statistical thermodynamic formula [4]

$$\alpha^2 = kT^2 C, \quad (3)$$

where C = heat capacity of degrees of freedom of the type considered in the volume l^3 ; d^3 = mean volume occupied by one particle; and the energy E satisfies the condition

$$E \gg kT, \quad (4)$$

where q = relative concentration of the substance responsible for the process considered.

The mean number of elementary acts of the process considered in a uniform system with volume V is calculated according to the formula [1]

$$N = \frac{V}{l^3} W = q \frac{V kT}{l^3 \hbar} \exp \left\{ \frac{E^2}{2\alpha^2} \right\} \exp \left\{ -\frac{E}{kT} \right\}. \quad (5)$$

It has also been shown that Eqs. (1) and (5) may be written in the form [1]

$$W = q \frac{kT}{\hbar} \exp \left\{ -\frac{E}{kT_{\text{ef}}} \right\} \quad (6)$$

$$N = q \frac{V k T}{l^3 \hbar} \exp \left\{ - \frac{E}{k T_{\text{ef}}} \right\}, \quad (7)$$

where T_{ef} may be determined from the formula

$$T_{\text{ef}} \approx T \left(1 + \frac{E}{2CT} \right). \quad (8)$$

In this communication we discuss the results obtained and some possible physical causes leading to the relationship between the preexponential factor and the activation energy in the experimental equation for reaction rates

$$K = K_0^n \exp \{ \beta E_a^n \} \exp \left\{ - \frac{E_a}{RT} \right\}, \quad (9)$$

where K_0^n is independent of E , and n is a quantity varying from 0.5 to a few units [1, 2]; R = gas constant. In what follows, as in the previous communication [1], the calculation is only carried as far as orders of magnitude.

Formulas for the determination of ΔT_{ef} . Equations (6) to (8) show that the rate of the process may be depicted by a simple formula of the type of the Arrhenius formula, with a preexponential factor independent of E ; but in this case the temperature considered is not the mean temperature of the system, T , but some effective temperature $T_{\text{ef}} > T$, and dependent upon E . It follows from (8) that the temperature T_{ef} differs from T by the quantity

$$T_{\text{ef}} - T = \Delta T_{\text{ef}} = \frac{E}{2C} = \frac{E}{2CT} \cdot T \quad (10)$$

We compare the quantity ΔT_{ef} with the mean fluctuation of temperature in the region l^3 given by [4]:

$$[(\overline{\Delta T})^2]^{1/2} = T \sqrt{\frac{k}{C}} \quad (11)$$

Introducing (3) and (11), we may write Eq. (10) in the form

$$\Delta T_{\text{ef}} = \frac{T}{2} \sqrt{\frac{k}{C}} \cdot \frac{E}{\alpha} = \frac{E}{2\alpha} [(\overline{\Delta T})^2]^{1/2} \quad (12)$$

We may proceed in the following way with the problem of determining the value of ΔT_{ef} . According to [2, 3, 5]

$$\frac{L^2}{d^2} \leq \left(\frac{E}{kT} \right) \left(\frac{d}{\gamma \lambda} \right); \quad \frac{L^3}{d^3} \gg \frac{E}{\gamma kT}, \quad (13)$$

where $\lambda = \hbar v / kT$. On the other hand, the heat capacity C of the region l^3 may be presented in the form

$$C = \gamma C_0 \frac{L^3}{d^3}, \quad (14)$$

where C_0 = heat capacity on the basis of a single degree of freedom. If account is taken of the fact that $(Ed/\gamma \hbar v)$ is a large number, then Eqs. (13) and (14) give rise to the inequality

$$C_0 \frac{E}{kT} < C < \frac{C_0}{V \gamma} \left(\frac{Ed}{\hbar v} \right)^{3/2} \quad (15)$$

or

$$C_0 \frac{E}{kT} < C < \frac{C_0}{V \gamma} \left(\frac{E}{kT} \right)^{3/2} \left(\frac{d}{\lambda} \right)^{3/2}, \quad (15a)$$

Then, by means of (15) and (15a) we obtain from (10) the inequality

$$\frac{T}{2} > \Delta T_{ef} > \frac{T}{2} \cdot \sqrt{\frac{kT}{E}} \left(\frac{\lambda \gamma^{1/2}}{d} \right)^{1/2}, \quad (16)$$

which permits of the drawing of definite conclusions concerning the size of ΔT_{ef} .

Equations for the determination of the preexponential factor, $\exp(E/2\alpha^2)$. Equations (1) and (5) show that the rate of the activation processes depends on the compensating quantity

$$\exp \left\{ \frac{E^2}{2\alpha^2} \right\},$$

which may play an appreciable role only when

$$\frac{E^2}{2\alpha^2} > 1, \quad (17)$$

where the inequality denotes that $E^2/2\alpha^2$ is a quantity of the order of some units or greater.

To estimate the ratio $E^2/2\alpha^2$ we make use of Eqs. (3) and (15a); by this means we obtain the inequality

$$\left(\frac{\lambda}{d} \right)^{1/2} \frac{\sqrt{\gamma E k}}{2C_0 T^{1/2}} < \frac{E^2}{2\alpha^2} < \frac{E}{2C_0 T}$$

or (if $C_0 \approx k$)

$$\sqrt{\frac{E}{kT}} \left(\frac{\lambda}{d} \right)^{1/2} \frac{\sqrt{\gamma}}{2} < \frac{E^2}{2\alpha^2} < \frac{E}{2kT} \quad (18)$$

These relationships limit the magnitude of $E^2/2\alpha^2$ on both sides.

In addition, it is possible to obtain one more useful inequality, if account is taken of the fact that

$$\left(\frac{Ed}{\hbar v \gamma} \right)^{1/2} = \left(\frac{E}{kT} \right)^{1/2} \left(\frac{d}{\lambda \gamma} \right)^{1/2} \ll \left(\frac{E}{kT} \right)^2 \left(\frac{d}{\lambda \gamma} \right)^2 \quad (19)$$

Then, by means of (3), (14), (2) and (19) we obtain (if $C_0 \approx k$)

$$\alpha^2 = \gamma k^2 T^2 \frac{l^3}{d^3} \ll \gamma (kT)^2 \left(\frac{E}{kT} \right)^2 \left(\frac{d}{\gamma \lambda} \right)^2 \quad (20)$$

from which there arises the inequality

$$\frac{E^2}{2\alpha^2} \gg \left(\frac{\lambda}{d} \right)^2 \left(\frac{\gamma}{2} \right) \quad (21)$$

The inequality so obtained makes it possible to proceed to the estimation of the ratio $E^2/2\alpha^2$, and so to the pre-exponential factor $\exp(E/2\alpha^2)$ in Eqs. (1) and (5). For what follows it is useful to present the ratio $E^2/2\alpha^2$ in the form of the product of two quantities

$$\frac{E^2}{2\alpha^2} = \frac{E}{2CT} \cdot \frac{E}{kT}, \quad (22)$$

one of which, $E/kT \gg 1$, and the other, $E/2CT < 1$. According to (10) it is possible to rewrite (22) also in the form

$$\frac{E^2}{2\alpha^2} = \frac{\Delta T_{ef}}{T} \cdot \frac{E}{kT}, \quad (23)$$

Some causes of the compensation effect. The relationship obtained above make it possible to understand some general kinetic causes leading to the relationships observed for the preexponential factor in processes and systems of various kinds. A qualitative physical explanation of one of the causes giving rise to the compensation effect may be obtained in the following way. As has been noticed in [1, 3], the elementary act of the activation process seems to consist of two stages: the first, roughly speaking, can be referred to some "heated" region l^3 at a temperature $T(U)$ (depending on the "instantaneous" values of the energy U in this region) through exchange of energy with other particles in the system. The second stage consists in each local instantaneous temperature $T(U)$ corresponding to some probability, not equal to zero, that the energy $E' \geq E \gg kT$ is collected by chance into individual bonds, which leads to their disruption. This second stage, however, if it takes place, is carried out at some local temperature $T(U)$, which is generally different from the mean temperature T of the system. Calculation shows that the overwhelming majority of individual processes are carried out within the region l^3 at a local temperature $T_m \approx T + E/C$, corresponding to the maximum probability of the individual act [1-3]. The temperature T_m corresponds to an energy U_m which exceeds the mean energy \bar{U} by a magnitude approximately equal to E ; i.e., $U_m \approx \bar{U} + E$ [3]. This signifies, that in the great majority of cases, when the energy $E' \geq E \gg kT$ is collected by chance into individual bonds of the region l^3 , the remaining degrees of freedom of the volume l^3 possess approximately the mean energy. The fact that the mobilization of energy $E' \geq E$ proceeds fundamentally in "heated" volumes l^3 , leads to increase in the conditional probability $W(E/U)$ of the act of concentration of the energy $E' \geq E$, in individual degrees of freedom, which is due to the favorable local instantaneous conditions existing at a given moment in this region l^3 , from which it is possible to draw directly the energy $E' \geq E$ necessary for the individual process. The increase in $W(E/U)$ when $U = U_m$ is not completely compensated by decrease in the probability $W(U_m)$ of the "hot" region l^3 at temperature T_m . This leads also to the development of a peak in the function $W(E/U)$. $W(U)$, which determines the probability of the individual act [1, 3]. Because of the fact that the local temperature T_m , corresponding to the maximum probability of the occurrence of the individual act of the activation process, depends on the activation energy E , a more complex relationship arises between the rate of the process and the activation energy in comparison with the simple Arrhenius formula.

Formulas (6) to (8) show that if the formula for the rate of the process is converted to the usual "Arrhenius" form, the rate of the reaction is characterized not by the mean temperature of the system T , but by some effective temperature T_{ef} , which exceeds the mean temperature by a quantity ΔT_{ef} , which is determined by formulas (10), (12) and (16). T_{ef} is connected with T_m by the relationship

$$T_{ef} = \frac{T + T_m}{2} \quad (24)$$

If the "addition" ΔT_{ef} is not small, it may greatly increase the value of the rates of processes given by formulas (6) to (8) in comparison with the usual Arrhenius equation. In estimating ΔT_{ef} we take into account that the condition for the simultaneous occurrence of the inequalities (2) has the form [5]:

$$\sqrt{\frac{kT}{E}} \left(\frac{\gamma^{1/3} \lambda}{d} \right)^{1/2} \ll 1 \quad (25)$$

On the other hand, the right hand part of the inequality (16) is converted to the form

$$\frac{\Delta T_{ef}}{T/2} > \sqrt{\frac{kT}{E}} \left(\frac{\lambda \gamma^{1/3}}{d} \right)^{1/2}, \quad (25a)$$

where the right hand part (25a), according to (25), is considerably less than 1. Comparing the inequalities (25), (25a) and the left hand part of (16), we see that the magnitude of ΔT_{ef} may be appreciable, since the condition

$$\Delta T_{ef} = T_{ef} - T \ll \frac{T}{2} \quad (26)$$

is not in contradiction with the method employed. But the possibility of fulfilling Eq. (26) means that in the formulas (6) and (7), which determine the rate of the activation process, the temperature T_{ef} is introduced, which may exceed the mean temperature system by some tens of degrees (since, for example, when $T = 300^\circ K$ the quantity $T/2 = 150^\circ$). This, on its part, leads to the fact that the rate of the processes are considerably greater than would follow from the simple Arrhenius formula.

We come to the same conclusion also, by analysis of formulas (1) and (5), simultaneously with the relationships (18) and (21) to (23). Actually, from (1), (5) and (23) it follows that if the ratio $\Delta T_{ef}/T$ is not very small [which, according to (26), is possible], the preexponential factor $\exp(E^2/2\alpha^2)$ will be large and its compensating effect will be considerable. This result is also arrived at from the fact that according to formula (22) the ratio $E^2/2\alpha^2$ is the product of two factors

$$\frac{E}{2CT} < 1 \text{ and } \frac{E}{kT} > 1.$$

then if

$$\frac{2CT}{E} < \frac{E}{kT}, \quad (27)$$

then the product

$$\frac{E}{kT} \cdot \frac{E}{2CT}$$

may be considerable, which means the development in formulas (1) and (5) of a large preexponential factor. For example

$$\frac{E}{kT} = 100 \text{ and } \frac{E}{2CT} = 0,2$$

we obtain $E^2/2\alpha^2 = 20$, and the factor e^{20} enters into the preexponential factor. Relationships (18) and (21) show that the development of that part of the compensation effect here considered permits of larger values of E , increase in the rate V of the energy transfer, decrease in the magnitude d , and consequently increase in the density $\rho \sim 1/d^3$; and, finally increase in the number of degrees of freedom γ in the volume d^3 , and therefore, in unit volume also. The second, third and fourth conditions show that in solid bodies there exist the most favorable conditions for attaining that part of the compensation effect derived in the present work, since usually in solid bodies the rate v of the transfer of energy and density is large.

The temperature relationship of the preexponential factor, $\exp(E^2/2\alpha^2)$. The formulas obtained make it possible to calculate that the ratio $E^2/2\alpha^2$, and therefore the factor $\exp(E^2/2\alpha^2)$ depend, generally speaking, on the temperature; but, as we shall see below, this relationship, compared with the quantity $\exp(-E/kT)$ is of little significance. Actually, it is usual to describe the experimental data by constructing a graph of the logarithm of the rate of the process against $1/T$. The rate of the process is expressed by formula (5). If we take logarithms of (5) and introduce the notation $Z = \ln N$ and $X = 1/kT$, we obtain the equation, taking account of (3),

$$Z - A - \frac{kE^2}{2C} X^2 = -EX \text{ or } Z - A = -EX \left(1 - \frac{kE}{C} X \right) \quad (28)$$

where

$$A = \ln \frac{V k T q}{l^3 h}$$

The equations (28) may be presented in the form

$$Z - Z_0 = -XE \text{ or } Z - A = -BEX \quad (29)$$

where

$$Z_0 = A + \frac{kE^2}{C} X^2; \quad B = 1 - \frac{kE}{C} X \quad (30)$$

If Z_0 and B did not depend on $1/T$ (where $E = \text{constant}$) equation (29) could be presented respectively in coordinates (X, Z) as equations of straight lines passing through the points (O, Z_0) and (O, A) , with slopes of $(-E)$ and $(-BE)$ [6]. Also if Z_0 did not depend on E , the first of these equations (29), in the coordinates (X, Z) could be presented as a family of straight lines (for different values of E), with a focus at (O, Z_0) [6]. In reality Z_0 and B depend on both T and E . But this relationship is masked by the fact that

$$A \gg \frac{kE^2}{C} X^2 \text{ and } \frac{E}{C} X < 1 \quad (31)$$

For example, at ordinary temperatures, $kT \approx 4 \cdot 10^{-14}$ erg, and $E = 2.5 \text{ eV}$.

$$E^2 X^2 = \left(\frac{E}{kT} \right)^2 \approx 10^4.$$

For solid bodies, $v \approx 5 \cdot 10^5$ cm/sec; $d \approx 3 \cdot 10^{-8}$ cm; $\gamma \approx 3$; $q = 0.1$. Then according to (2) $l^3 \approx 10^{-20}$ cm³ and when $V \approx 1$ cm³ we obtain the relationship $A \approx \ln(10^{33.5}) \approx \ln e^{77} = 77$. On the other hand, from the left hand part of the inequality (15a) it follows that when $C_0 = k$,

$$\frac{k}{C} < \frac{kT}{E}; \quad B \approx 1 \quad (32)$$

and

$$\frac{k}{C} E^2 X^2 = \frac{k}{C} \left(\frac{E}{kT} \right)^2 < \frac{E}{kT} \quad (33)$$

The inequalities (32) and (33) lead to the relationship (31). On increase of temperature the quantities $E^2 \cdot X^2 = (E/kT)^2$ and kEX/C diminish, while the quantity A increases slowly, which results in an intensification of the inequality (31). Thus, Z_0 consists of two components, the one of which is greater than the other and independent of T . Therefore, with change in temperature, the quantity $Z_0 = A - (k/C) \cdot E^2 X^2$ changes relatively slowly. At the same time the quantity $X \cdot E = E/kT$, which stands in the right hand portion of (29), changes in reverse proportionality to T . Therefore for changes in temperature which are not too great, the dependence of Z_0 and B on T can, with essential accuracy, be regarded as slight. In this connection the experimental data can, with a considerable accuracy be represented on a straight line with slope of $-E$. Deviations from the straight line, may, apparently, be found when the temperature is changed over a wider range. Thus, on graphs constructed in polylogarithmic coordinates ($\ln N, 1/T$) in a given experiment, the deviation from the straight line under ordinary conditions will be of little significance since we are using not the velocities themselves, but their logarithm.

In direct calculation of rates of reaction according to formula (5), where the exponential functions themselves and not their logarithms, are used the factor $\exp(E^2/2\alpha^2)$, which satisfies the condition

$$\exp \left\{ \frac{E^2}{2\alpha^2} \right\} \ll \exp \left\{ \frac{E}{kT} \right\}, \quad (34)$$

may diminish these velocities by several orders of magnitude.

DISCUSSION

The results obtained in this and previous communications [1, 2] permit of an explanation of some causes operating to produce the strong dependence of the preexponential factor on the activation energy in formulas for reaction rates on the basis of quite general premises. The applicability of the relationships found is limited by the generality of the assumptions made in arriving at them, as discussed in the previous communication [1]. It should also be emphasized that in this study of the compensation effect only pure thermal activation processes have been considered, and the effect of external effects (electrical, mechanical, etc.) have not been taken into account. The compensation effect has also been observed, however, in processes occurring in bodies submitted to the influence of external fields. Thus in [7] the compensation effect arising in the study of dielectric loss in organic compounds with long chains has been considered. The effect was very great, since the free exponential factor had a value of 10^{25} .

Similar effects to a greater or less degree are also to be expected in other phenomena, depending upon activation processes which take place under the influence of external fields (ionic conductivity, electronic conductivity of semiconductors, etc.). In a number of cases the compensation effect has been observed in these phenomena, as we have remarked in [2], where the corresponding references to the literature were given. In this connection the question arises about general causes producing the compensation effect in systems exposed to external fields. Some new possibilities in this direction are opened up by the statistical method of calculating the rate of activation processes set out earlier by one of the present authors [3] for the case of condensed bodies under the effect of external fields.

It was shown in [3] that for a considerable range of conditions the external field may be considered as a perturbation, which suggested the possibility of using the ideas of the thermodynamical "theory of perturbations" [4]. By this means it was possible to obtain on a statistical basis formulas to calculate the rates of activation processes taking place in alternating and in constant external fields, without having recourse to detailed mechanical models and methods of mechanics. In addition, certain further possibilities for the explanation of the compensation effect appeared, taking account of the correlation between various regions with volumes $\approx l^3$, which we had hitherto neglected [1, 3].

In some cases the observed correlation may be estimated quantitatively by means of the correlation theory of stationary chance processes, on the basis of statistical models, as set out in [3, 5, 8]. It could be shown that this introduces a considerable change in the nature of the relationship between K_0 and E . A detailed investigation of this question has acquired considerable importance, since works have recently appeared calling attention to the important role played by collective effects in the compensation effect in the formation of high value preexponential factors. In particular, Semenov has shown the probability of such processes in the fast low temperature polymerization in the solid phase [9] (Tal'roze, Blyumenfel'd, et al); a large compensation effect has been discovered, with great variations in K_0 for the electrical conductivity of organic polymers [10]. Australian authors have described similar phenomena for the kinetic orientation of polymers in high frequency fields [7].

SUMMARY

1. An explanation has been given of some general stastico-kinetic causes, leading to a strong dependence of the preexponential factor in formulas for the rate of activation processes on the activation energy, and the corresponding formulas have been derived.

2. It has been shown that because of the localization of the overwhelming majority of elementary acts of the activation processes in macroscopically small regions possessing "instantaneous" temperature considerably in excess of the mean temperature of the system, and depending on the activation energy, in the expressions for the rate constant a strong relationship is revealed between the preexponential factor and the activation energy. Conditions typical for condensed systems have been established, which favor the appearance of a considerable preexponential factor.

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FORMATION OF UNSTABLE FORMS OF PHTHALOCYANINES AND HEMATOPORPHYRIN DURING FLASH ILLUMINATION

A. N. Terenin, E. B. Lyubomudrov, and A. V. Shabliya

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Spectroscopic investigation of the changes in chlorophyll and phthalocyanine solutions under the influence of light of high intensity [1] established their reversible bleaching. This effect is usually ascribed to an accumulation of the excited molecules at the metastable triplet level. However in the present work the possibility of a transitory reversible photoreaction with the solvent has also been examined.

EXPERIMENTAL

During, and after carrying out the present investigation there appeared many papers concerned with the flash photochemistry of chlorophyll and dyestuffs [2]. There was only one reference concerning phthalocyanine in the literature [3], and no information at all concerning hematoporphyrin.

The principal shortcoming of the previous laboratory investigation was the use of a photographic method. In the present work a photoelectrical method has been used similar to that described in the literature [4]. Light from an incandescent lamp (6 v, 100 w), fed by a constant current, passing through a 15 cm long cell holding the solution, as a parallel beam was focussed on the inlet slit of the UM-2 monochromator (or ISP-51), which was set at the required wavelength. To the exit slit was attached a FEU-32 photomultiplier, the signal from which was fed into a IO-III B oscillograph. The cell was placed at the axis of a spiral quartz lamp with a flash energy of 1000 joules.

In order to reveal changes in the absorption spectrum of the studied solution at the moment of the flash two curves were recorded at the assigned wavelength, successively, on the oscillograph screen. The first curve, giving only the parasitic scattered light from the flash discharge lamp falling on the slit of the monochromator, was photographed without admitting light from the incandescent lamp into the monochromator. The second curve was produced during a flash of the flash-discharge lamp and passed into the monochromator with constant light from the incandescent lamp. If at the moment of the flash there has occurred a change in the absorption of the studied material at the given wavelength, then the second curve on the oscillograph screen will be either displaced downwards (in the case of an increase in absorption) or displaced upwards (in the case of a decrease in absorption). If however changes in the light transparency have not occurred then the second curve will be identical with the first.

In order to obtain data on the spectral change at each separate wavelength, four measurements were made: 1) The light current from the incandescent lamp as a vertical kick on the oscillograph screen; 2) the scattered light from the flash-discharge lamp with the studied material present and in the absence of light from the incandescent lamp; 3) the absorption of the material in light from the incandescent lamp; 4) the absorption of the material during flash-discharge while passing light from the incandescent lamp through it.

From these measurements the optical density curve (absorption spectrum) of the material under flash illumination was plotted. The amplitudes of the curves photographed from the screen of the oscillograph were measured by the increased scale on the screen, graduated in millimeters.

Experiments carried out with a solution of magnesium phthalocyanine in pyridine* (concentration of the order 10^{-6} M) freed from dissolved air by pumping showed that under the influence of flash-discharge a weakening of the main absorption band at 673 m μ , and the appearance of an absorption band in the 560 m μ region occurred. In experiments using the photographic method [1] the new absorption band was not detected, obviously because of inadequate photometric sensitivity. In the presence of dissolved air the new band did not appear. Typical curves

*Undried pyridine was used in the experiments, i.e., containing ~5% moisture.

produced on the oscillograph screen at different wavelengths of light passing through the solution are reproduced in Fig. 1. The absorption maxima for a solution of magnesium phthalocyanine in pyridine were at 673, 647 and 608 $m\mu$, of which the first had the highest intensity.

As seen from the oscillogram the reduction of absorption at 673 $m\mu$ and the appearance of a new absorption band at 560 $m\mu$ at the moment of the flash lasted 1–1.2 msec, where the flash duration of the flash-discharge lamp was 0.5–0.6 msec. After admitting air into the cell this effect disappeared, i.e., curves 1 and 2 on the oscillogram completely coincided (Fig. 2).

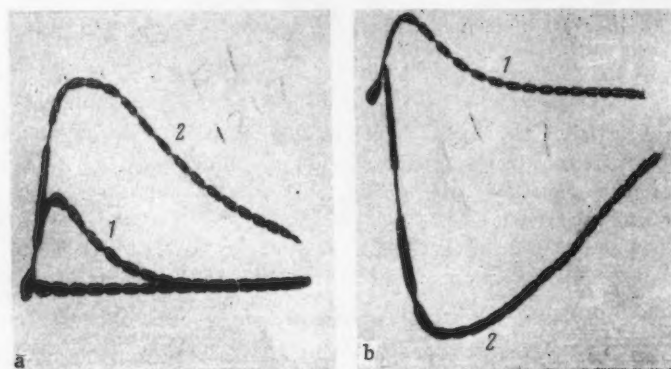


Fig. 1. Oscillographic evolutions of the transparency change of a solution of Mg-phthalocyanine in pyridine exposed to flash radiation, at specified wavelengths. Each segment on the curve corresponds to 100 μ sec. Curves 1 were produced during flash illumination without passage of light and reproduce the scattered light from the flash-discharge lamp in the cell. Curves 2 give the transparency change of the solution at the given wavelength during flash illumination. An upward kick on the oscillogram denotes a decrease, a downward kick an increase in absorption of the solution during flash illumination: a) at 673 $m\mu$; b) at 560 $m\mu$.

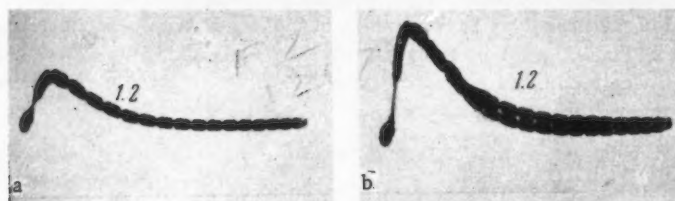


Fig. 2. Repetition of the experiment in Fig. 1 in the presence of air in the cells.

The changed spectrum of the solution of magnesium phthalocyanine in pyridine during exposure to the flash-discharge, measured exactly, is shown in Fig. 3 (curve 2); curve 1 gives the absorption spectrum of the same solution under the usual conditions.

Hematoporphyrin in air-freed pyridine (concentration 10^{-4} M) during flash illumination also exhibited a transitory change in the absorption spectrum (Fig. 4). This change, lasting 1.5 msec, consisted of the disappearance of the main absorption bands of hematoporphyrin at 425, 505, 540, 580, 630 $m\mu$ (curve 1) and the appearance of new absorption maxima at 470, 520, 605 and 660 $m\mu$ (curve 2)*. In contrast to the pyridine solution freed from atmospheric * The continuous spectral curves represented in Figs. 3 and 4 were measured on the SF-2M spectrophotometer, and the dashed curves in the flash-discharge apparatus with plotting of the spectrum exactly according to the method described above. Therefore comparison is only valid for the position of the absorption bands and not for the values of their optical densities D, which have values only for the continuous curves.

oxygen the spectrum of solutions of hematoporphyrin in water, methanol and glycerine did not change during flash illumination.

The reversible photoreduction of chlorophyll and other natural pigments, as well as of magnesium phthalocyanine in solutions containing reducing agents (ascorbic acid, phenylhydrazine, etc.), was studied in detail in investigations by Krasnobski and by Evstigneeva and co-workers [5-8]. Under the usual exposure conditions Krasnobski and co-workers detected in air-freed pyridine solutions of these pigments with reducing agent, a photoreduced form with an absorption maximum lying at 525-570 m μ depending on the pigment. This form was found to be a stable secondary stage of the reduction. The primary (unstable) photoreduced form of the pigment molecule was observed by Evstigneeva only in the case of pheophytin [6], protopheophytin and hematoporphyrin [7] at a lowered solution temperature (-40°). For pheophytin such a primary form has an absorption band at 440 m μ and a high maximum at 340 m μ prior to formation of the secondary reduced form with a band at 525 m μ . In the case of hematoporphyrin the primary photoreduced form of the pigment, according to Evstigneeva, has absorption at 460 m μ in the gap between the narrow absorption bands of hematoporphyrin.*

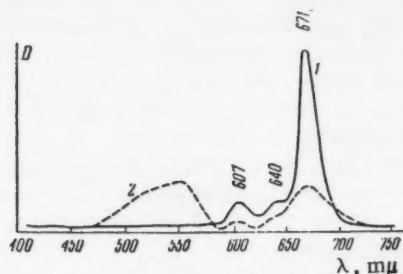


Fig. 3. Absorption spectra of a solution of magnesium phthalocyanine (concentration 10^{-6} M) in moist pyridine: 1) spectrum of original solution on SF2-M spectrophotometer; 2) the changed spectrum of the same solution during flash illumination, reconstructed from the oscillogram Fig. 1.

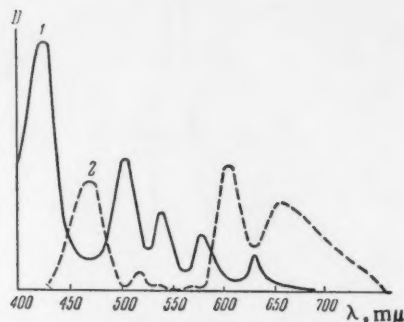


Fig. 4. Absorption spectra of a solution of hematoporphyrin in moist pyridine: a) spectrum of original solution (on SF-2M); 2) spectrum of the same solution during flash illumination.

The appearance in our experiment of a maximum at 470 m μ which was also located in the gap between the narrow absorption maxima of hematoporphyrin at 425 and 505 m μ indicated the formation of the primary reduced form of hematoporphyrin under flash illumination in the absence of the extraneous reducing agent (ascorbic acid) used in the work of reference [7]. Since, as was shown by our experiments, a solution of hematoporphyrin in water, dry methanol or glycerine did not give the same band under flash-discharge, then the formation of the primary reduced form cannot be due to the acceptance of hydrogen from the pyridine with dehydrogenation of the latter. From Evstigneeva's [8] potentiometric measurements it followed that the primary form of photoreduced pigments is an electrode activated negatively-charged semiquinone of the pigment. Therefore under our conditions the pyridine molecules function as a reducing agent by returning the electron to the hematoporphyrin molecule, excited by light. As pointed out above the excited molecules accumulate in the metastable triplet state. The 660 m μ absorption maximum detected here is in good agreement with the maxima of the second (stable) form of hematoporphyrin observed during photoreduction of the pigment with ascorbic acid in pyridine [7].

The primary semi-reduced form of the radical-anion, i.e., the negatively charged semiquinone of the pigment, we still designate $\cdot P_{cy}^-$ for magnesium phthalocyanine and $\cdot H_p^-$ for hematoporphyrin. According to Krasnobski and Evstigneeva [5] the secondary (stable) form is a neutral radical, the semiquinone of the pigment, which is formed from the negatively charged semiquinone by addition of a proton from the reducing agent (ascorbic acid), i.e., $\cdot P_{cy}^- + H^+ = \cdot P_{cy} - H$ and $\cdot H_p^- + H^+ = \cdot H_p = H \cdot$.** In pyridine solution, under our conditions, separation of a proton from the pyridine molecule is excluded, and therefore if the interpretation of the nature of the secondary form of the pigment is correct, then the source of the proton can only be water molecules associated with the strong base pyridine.

*See Fig. 3 in reference [7].

**It is possible however that the secondary form is a dimer formed from two such radicals.

In fact from Sidorov's work in our laboratory [9] it follows that in one of the two types of association of water with pyridine, the molecule of H_2O is added by one of its own H atoms to the pyridine molecule, and consequently its second H atom may be protonized.*

Thus, under the conditions of flash illumination, observation of the spectra of the primary form of the pigment did not require either the presence of an extraneous reducing agent or a lowering of the solution temperature, as was necessary to produce this form under the usual conditions [7]. The explanation of this may be sought in the very much greater concentration of triplet molecules of pigment produced in the flash-discharge apparatus. The presence of molecules in the triplet state can apparently be deduced from the appearance of the high intensity absorption maximum at $605 m\mu$. The functioning of pyridine as an electron donor is not unusual. Thus in our laboratory Arvan established that methylene blue is easily and reversibly photo-reduced during ordinary illumination in pyridine solution freed from air.

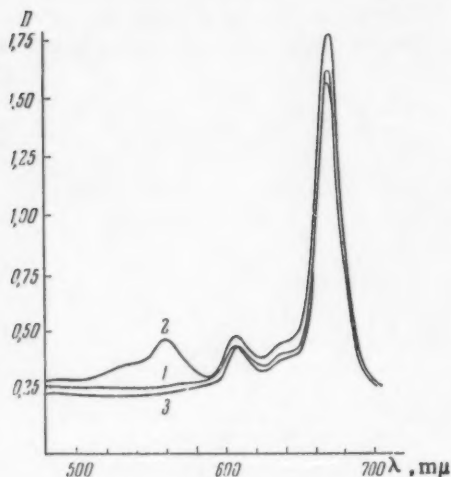


Fig. 5. The absorption spectra of a solution of magnesium phthalocyanine (concentration 10^{-4} M) in pyridine freed from atmospheric oxygen, with addition of an aqueous solution of $MgSO_4$: 1) original spectrum at -40° ; 2) after irradiation by 15 flashes without a light filter from four IFK-500 flash-discharge lamps (at -40°); 3) after warming the solution to 20° .

In the case of Mg phthalocyanine in pyridine under flash illumination (Fig. 3) there appeared only the absorption maximum at $560 m\mu$ of the stable ("red") form, observed in the presence of a reducing agent under ordinary illumination [5]. It is possible that in view of the limitation of the spectral region to the range $450-750 m\mu$ the band of the primary form could not be detected here. In fact during our investigation of the dark addition of electrons from metallic sodium to Mg phthalocyanine there was observed in addition to the $53-570 m\mu$ band of the secondary form, also a maximum at $950 m\mu$ [10] apparently belonging to the primary form of the pigment molecule, to which was added an electron (radical-anion $\cdot P_{cy}^-$). By analogy with pheophytin an absorption maximum in the shortwave region at $400 m\mu$ could also be expected for the primary form, which was outside the range of the present apparatus.

In order to detect photoproducts originating during short-wave ultraviolet irradiation (without flash-discharge), experiments were carried out with a solution of magnesium phthalocyanine in an alcohol-ether mixture at -180° under vacuum.** In the absorption spectrum taken after illumination, only the appearance of a small band at $700 m\mu$ was detected, which disappeared during thawing out. In the rest of the region ($400-650 m\mu$) there were no observable changes.

Experiments carried out at -180° but with addition of pyridine to the alcohol-ether solution of Mg phthalocyanine (15% by volume), after 2 hr exposure to the full light of a projection incandescent lamp (12 v, 100 w) disclosed an absorption band at $530-560 m\mu$, belonging to the secondary photoreduced form of the pigment, although in our experiments reducing agents, except for pyridine were clearly absent.*** The $700 m\mu$ band was absent.

Check experiments carried out with a solution of Mg phthalocyanine in pyridine only showed that the formation of the product with a maximum at $530-570 m\mu$, during irradiation with full light from four IFK-500 flash-discharge lamps with chilling at -40° , took place only in pyridine solutions containing a small percentage of dissolved water. Irradiation, under analogous conditions, of solutions of Mg phthalocyanine in pyridine subjected to careful drying, did not give rise to new maxima in the spectrum. This result agrees with the results of paper [11], in which, however, ascorbic acid was introduced into the pyridine solutions as a reducing agent. In analogous experiments

*The presence of protons in the moist pyridine also follows from the fact that the weak maximum at $520 m\mu$ (Fig. 4) appearing during flash-discharge exposure of hematoporphyrin in pyridine coincides with the weak maximum of the spectrum of the semireduced form of the pigment observed in 1 N H_2SO_4 during photoreduction with ascorbic acid [5].

** A solution of magnesium phthalocyanine in an ethanol and ether (2:1) mixture of concentration $10^{-4} - 10^{-3}$ M was poured into a 1 mm quartz cell, the back surface of which was itself an aluminum mirror cooled by liquid air. Illumination was made with the full light from a 5VD-120A lamp during two hours at -180° . Measure of the absorption spectra of the frozen glassy solution were made after exposure on the SF-2M spectrophotometer by reflected light.

*** Ethanol did not show a reducing action judging by the previous experiment.

carried out with chlorophyll (a + b), phenophytin (a + b), ethylchlorophyll (a + b) in pyridine, diethyl ether, acetone and quinoline with addition of water, we did not observe any changes in the absorption spectrum after illumination at -40° .

Mg, Al and other cations exert a strong influence on the water molecules associated with them in the hydration sheath, displayed by the decrease in the frequency of the antisymmetric valence vibration of the H_2O molecule [12]. Therefore a series of experiments was carried out with a pyridine solution of magnesium phthalocyanine to which 3-5% by volume of saturated aqueous solutions of Mg, Al, Nd, Ce sulfates were added. Irradiation was carried out in an evacuated glass cell at -40° . The intensity of the illumination was increased (4 IFK-500 flash lamps). Introduction of the cations mentioned above increased the concentration of the generated photoreduced secondary form by 5-7 times. Two absorption maxima were observed; a main band at $560 m\mu$ and subsidiary bands at 530-540 $m\mu$ (Fig. 5). In the experiments described above, when measurements of the spectrum were made through an appreciable period of time after flash illumination the original pigment was already regenerated to a considerable degree as seen from Fig. 5. Bringing the solution to 20° or introduction of air completely remove the absorption maxima in the 530-560 $m\mu$ region of the secondary reduced form of the pigment.

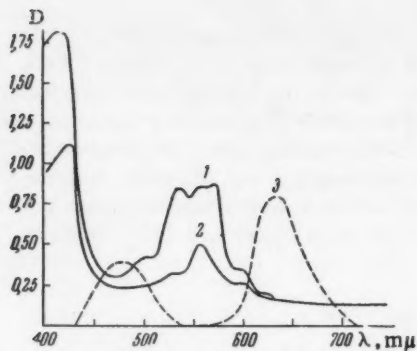


Fig. 6. Absorption spectra of a solution of hematoporphyrin in glacial acetic acid: 1) spectrum of a fresh solution in air; 2) after subjection to a vacuum; 3) spectrum during flash irradiation (reconstructed from the oscillograms).

In the experiments described above, illumination was made with the full light of the flash-discharge lamps, i.e., excitation of the pigments was also carried out in the region of the ultraviolet absorption band in contrast to the usual experiments on photoreduction in which only red light is used.

Hematoporphyrin has the properties of a spectroscopic acid-base indicator, i.e., the position of the narrow bands in absorption and luminescence changes during addition and removal of a proton [13]. In connection with our experiments on a proton phototransfer

[14] it was of interest to examine whether under conversion of the pigment molecule into the triplet state, a separation of the proton from the nitrogen atoms of the tetrapyrrole ring, or, on the contrary, an increase in the basic properties of the nitrogen atoms of the pyrrole rings with respect to a weak acid occurred at the moment of the flash-discharge.*

During flash irradiation of a solution of hematoporphyrin in anhydrous methanol freed from atmospheric oxygen by pumping out, a change in the absorption spectrum in the visible region was not observed. In contrast to the pyridine solution. On addition to the methanolic solution of hematoporphyrin of a small amount of hydrochloric acid (6 drops of concentrated HCl to 60 cm^3 of solution) the spectrum sharply changed its structure owing to addition of a proton to the nitrogen atoms of the pyrrole rings. The absorption bands at 500, 534, 572 and 624 $m\mu$ disappeared and new bands arose, a main peak at 553 $m\mu$ and subsidiary maxima at 524 and 594 $m\mu$ (for example, Fig. 6, curve 2). During flash illumination broad absorption bands appeared with maxima about 480 and 630 $m\mu$, and the original bands of the solution were reduced or disappeared. The duration of this change in the spectrum was of the order 1 msec. Subsequent measurement of the spectrum of the solution on the SF-2M spectrophotometer did not reveal residual irreversible changes in the solution. On introduction of atmospheric oxygen into the cell this effect, as usual, completely disappeared.

An analogous effect is observed for a hematoporphyrin solution in glacial acetic acid freed from air. The spectrum of the protonated pigment with maxima at 553, 524, 594 $m\mu$ disappeared during the flash-discharge, with the emergence of two new absorption bands around 480 and 640 $m\mu$ (Fig. 6). However in glacial acetic acid this change in the spectrum was partly irreversible, since after carrying out a number of flash-discharges the band maxima were decreased compared to the original spectrum.

On addition of a small amount of pyridine to the acetic acid solution of hematoporphyrin the spectrum assumed the form represented by curve 1 (Fig. 6). By exposure of such a solution to flash-discharge radiation the effect observed in the hematoporphyrin solution in glacial acetic acid occurred.

* Recently an experiment utilizing flash illumination of other substances in order to measure the constant of the rapidly established acid-base equilibrium with excited (in singlet state) molecules was described by Weller [15].

Thus protonated hematoporphyrin in an acid medium (glacial acetic acid or methanol with HCl) under flash illumination, instead of the original spectrum of its protonated form disclosed two maxima at 480 and 640 m μ . The position of the new absorption maxima which appeared in the spectrum could not be established with greater precision by the photoelectric method of measurement used by us. The maximum at 480 m μ mentioned above practically coincided with the 470 m μ maximum, and the second at 640 m μ with the 660 m μ maximum, observed in the pyridine solution of hematoporphyrin (Fig. 4). In addition the different nature of the medium in both cases must be taken into consideration. This implies that in acid media the same originators of the spectrum are formed as in moist pyridine, namely the negatively charged semireduced form (radical-anion) and the neutral radical, designated above $\cdot\text{H}_p^-$ and $\cdot\text{H}_p\text{H}$ ($\cdot\text{H}_p^- + \text{H}^+$).

The appearance of the same two forms in acid solution without an extraneous reducing agent must mean that acetate ions or nondissociated molecules of acetic acid as well as methanol molecules may act as electron donors. Addition of a proton to the semiquinone $\cdot\text{H}_p^-$ and formation of a neutral semiquinone $\cdot\text{H}_p\text{H}$ in the given solvents was known to be provided by the medium. The question remains open as yet as to whether photoreduction occurs only of the neutral nonprotonated molecules present in solution as a result of the acid-base equilibrium — the appearance of these semiquinones is then completely comprehensible, or whether the semiquinones $\cdot\text{H}_p^-$ and $\cdot\text{H}_p\text{H}$ arise from the protonated molecules HPH^+ . In the latter case the conclusion of the presence of a proton phototransfer process to the solvated sheath, preceding or concomitant with the transfer of an electron from the donor, is inevitable. Further investigation may possibly answer this question.

SUMMARY

1. In oxygen-free solutions of Mg phthalocyanine and hematoporphyrin in moist pyridine, as well as in acid media (CH_3COOH , $\text{CH}_3\text{OH} + \text{HCl}$), which were subjected to high intensity flash irradiation by visible light, transiently reversible photoreduced forms of these pigments arose in the absence of extraneous reducing agents.

2. These rapidly disappearing intermediate forms which were observed spectroscopically are attributed to reversible electron exchange between solvent molecules and light excited pigment molecules, which accumulated in the triplet metastable state.

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*Or even possibly a dimer of the latter $\text{HH}_p - \text{H}_p\text{H}$.

A STUDY OF REACTIONS OF ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM BY THE METHOD OF ISOTOPIC EXCHANGE

COMMUNICATION I. THE KINETICS OF THE REACTION OF ISOTOPIC EXCHANGE
IN PYRIDINE SOLUTION BETWEEN THE ETHYL ESTER OF α -BROMOMERCURY-
PHENYLACETIC ACID, AND MERCURIC BROMIDE LABELED WITH Hg^{203}

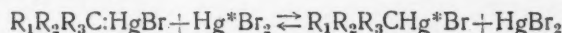
O. A. Reutov, V. I. Sokolov, and I. P. Beletskaya

The M. V. Lomonosov State University, Moscow

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The isotopic exchange of organomercury compounds with mercuric bromide is one kind of electrophillic substitution. As part of the general plan of investigating the reaction of electrophillic substitution at a saturated carbon atom we studied the isotopic exchange reaction



where $R_1 = H$; $R_2 = COOC_2H_5$; $R_3 = C_6H_5$, using absolute pyridine as a solvent. The kinetics of the reaction were studied over the concentration range for the reagents of 0.02-0.04 M/L at the temperatures 50, 60, 70 and 80°. The measurements were made by a method developed by us using paper radiochromatography [1].

EXPERIMENTAL

Alliquots of the organomercury compounds and mercuric bromide were dissolved separately in 2 ml portions of dry pyridine and brought to the temperature of the experiment. The temperature was maintained with a sensitivity of $\pm 0.1^\circ$. The moment when the solutions were mixed was taken as the beginning of the reaction. Samples were removed with a capillary and spotted on narrow paper bands impregnated with a 20% solution of ethylene glycol in acetone. The chromatograms were developed with a mixture of octane and benzene (3:2) and fixed with a solution of dithizone in chloroform. The papers were cut into strips and the activity of each of these was measured using a counter of type SI-2B and assembly B2, at a background of 40-50 counts/min. The degree of exchange was calculated from the formula

$$F = \frac{A_{Hg-ester}}{A_{HgBr_2} + A_{Hg-ester}} \cdot \frac{c_{HgBr_2} + c_{Hg-ester}}{c_{Hg-ester}}$$

where c is the concentration in M/L; A is the activity in counts/min.

In Table 1 are given the experimental data on the change with time of the degree of exchange for equimolecular ratios of the components at a constant temperature of 70°.

The values of the half-exchange time were determined from the graphs with coordinates $\log(1-F)$, t (Fig. 1), and the rate constants were calculated from these according to the equation for isotopic exchange

$$k = -\frac{\ln(1-F)}{(c_1 + c_2)t}$$

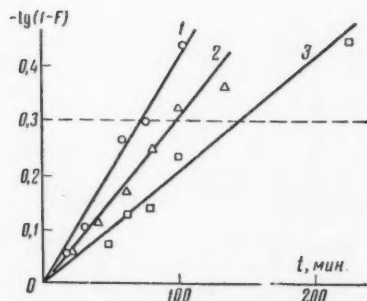


Fig. 1. The dependence of the kinetics of the isotopic exchange for various equimolecular concentrations of the components at 70°: 1) 0.04; 2) 0.03; 3) 0.02 M/L.

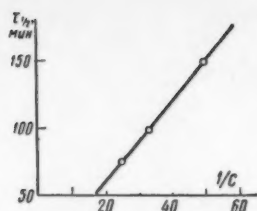


Fig. 2. The dependence of the period of half-exchange on the reciprocal concentration.

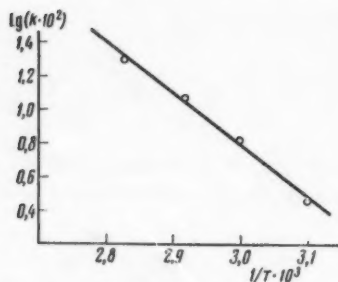


Fig. 4. The dependence of the logarithm of the rate constant of the reaction on the reciprocal temperature.

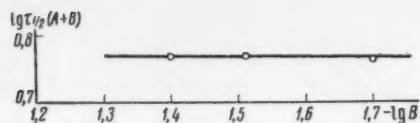


Fig. 3. The dependence of $\lg \tau_{1/2} (A + B)$ on $-\lg B$, illustrating a first order reaction for the organomercury compound.

The good linear dependence of the half-exchange time on the reciprocal value of the concentration (when $C_{\text{Hg}^* \text{Br}_2} = C_{\text{Hg-ester}}$) (Fig. 2) shows that the overall reaction is second order. For the determination of the order of the reaction applying to each of the components the exchange was carried out with various concentrations of the ester of α -bromomercurypheylacetic acid (0.02-0.04 M/L and a constant concentration of mercuric bromide (0.03 M/L) (Table 2).

The product of the half-exchange time and the sum of the concentrations in this case, too, remains constant (Table 3).

Figure 3 represents the graph of the dependence of $\lg \tau_{1/2} (A + B)$ on $-\lg B$, where the tangent of the angle of inclination gives the value $1-B$, in agreement with equation

$$\lg \tau_{1/2} (A + B) = \lg \frac{0.693}{k} + (1 - \alpha) \lg A + (1 - \beta) \lg B$$

TABLE 1.

$C^+ \text{Hg}^* \text{Br}_2 = C_{\text{Hg-ester}}$ M/L	t, min	$A \text{HgBr}_2$ counts per min	$A \text{Hg-ester}$ counts per min	F, %	$\tau_{1/2}$, min	$K_2 \cdot 10^2$ liters/M-min
0,04	15	510	30	11,1	74	11,7
		544	36	12,4		
	30	437	52	21,4		
		465	53	20,5		
	60	565	165	45,2		
		558	167	46,0		
0,03	75	368	121	49,5	98	11,8
	105	264	123	63,8		
	20	309	21	12,7		
	35	409	52	22,6		
	60	642	126	32,8		
	80	320	89	43,8		
0,02	100	274	99	53,1	145	11,7
	135	289	116	57,3		
	45	374	32	15,8		
	60	300	44	25,6		
	75	553	86	27,0		
	100	367	95	41,1		
	225	246	118	64,8		

TABLE 2

$C_{\text{Hg} \cdot \text{Br}_2}$ M/L	$C_{\text{Hg-ester}}$ M/L	t, min	A_{HgBr_2} counts per min	$A_{\text{Hg-ester}}$ counts per min	F, %	$\tau_{1/2}$, min	$K_2 \cdot 10^2$ (liters/M-min)
0,03	0,02	30	5460	374	16,1	117	11,8
		60	2845	274	22,0		
			2694	353	29,0		
		90	2360	401	36,3		
			1893	411	44,6		
0,03	0,03	125	1804	479	52,5	98	11,8
		20	309	21	12,7		
		35	409	52	22,6		
		60	642	126	32,8		
		80	320	89	43,8		
0,03	0,04	100	274	99	53,1	84	11,8
		135	289	116	57,3		
		20	1907	231	18,7		
			1842	188	16,2		
		50	1329	345	36,1		
			1689	499	39,9		
		80	1354	460	44,3		
			1326	537	50,4		
		110	989	570	63,9		

TABLE 3

C_{HgBr_2} (A)	$C_{\text{Hg-ester}}$ (B)	$\tau_{1/2}$, min	$\tau_{1/2}$ (A + B)
0,02	0,02	145	5,80
0,03	0,03	98	5,88
0,04	0,04	74	5,92
0,03	0,02	117	5,85
0,03	0,04	84	5,88

TABLE 4

c	temperature °C	t, min	A_{HgBr_2} counts per min	$A_{\text{Hg-ester}}$ counts per min	F, %	$\tau_{1/2}$, min	$K_2 \cdot 10^2$ (liters/ M-min)
0,03	50	70	1264	106	15,4	410	2,84
			1530	103	12,7		
		115	1462	159	19,6		
			1885	174	16,9		
		200	1455	258	30,2		
0,03	60		1540	243	27,2	176	6,60
		280	1499	362	38,4		
			1474	332	36,8		
		25	1921	86	8,6		
			2461	103	8,0		
0,03	70	50	2458	240	17,8	98	11,8
			2088	178	15,7		
		75	2257	322	25,0		
			1803	265	25,6		
		135	1640	416	40,5		
0,03	80		1636	411	40,2		
		170	1273	388	46,7		
			1916	645	50,3		
		20	309	21	12,7		
		35	409	52	22,6		
0,02	80	60	642	126	32,8		
		80	320	89	43,8		
		100	274	99	53,1		
		135	289	116	57,3		
		8	1454	83	10,8		
			2600	161	11,6		
			2036	218	19,3		
			2624	253	17,6		
			1606	282	29,9		

TABLE 4 (continued)

c	temperature °C	t, min	A _{HgBr₂} counts per min	A _{Hg-ester} counts per min	F, %	$\tau \frac{1}{2}$, min	$K_2 \cdot 10^2$ (liters/ M-min)
		50	1907	337	30,0	80	19,9
			1630	351	35,4		
			1820	433	38,4		
		60	1586	461	45,0		
			1370	314	37,3		

α and β give the order of the reaction for A and B. Consequently, the reaction is of first order for the organomercury compound; from this it follows that it must also be of first order for the mercuric bromide.

The values of the parameters of the Arrhenius equation are found from the graph of the dependence of the logarithm of the rate constant of the reaction on the reciprocal absolute temperature (Fig. 4) constructed from the data presented in Table 4; $\Delta = 16,3 \pm 1,0$ kcal/M, $\log A = 9,5$; the entropy of activation $\Delta S = 15,5$ entropy units.

SUMMARY

1. The kinetics of the isotopic exchange in pyridine solution between the ethyl ester of α -bromomercury-phenylacetic acid and Hg^*Br_2 at 50, 60, 70 and 80° were studied.

2. The reaction is bimolecular—first order for each component. The parameters of the Arrhenius equation were determined.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

A STUDY OF REACTIONS OF ELECTROPHILIC SUBSTITUTION
AT A SATURATED CARBON ATOM BY THE METHOD OF
ISOTOPIC EXCHANGE

COMMUNICATION 2. THE KINETICS OF THE REACTION OF ISOTOPIC EXCHANGE
IN AQUEOUS DIOXAN SOLUTION BETWEEN THE ETHYL ESTER OF α -BROMO-
MERCURYPHENYLACETIC ACID AND MERCURIC BROMIDE LABELED Hg^{203}

O. A. Reutov, V. I. Sokolov, and I. P. Beletskaya

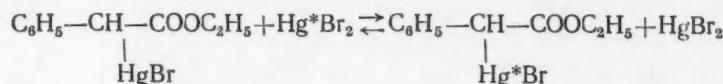
The M. V. Lomonosov State University of Moscow

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 7, pp. 1217-1222, July, 1961

Original article submitted November 19, 1960

The study of the isotopic exchange between the ethyl ester of α -bromomercuri-phenylacetic acid and mercuric bromide was begun by us several years ago. The conclusion was reached that the reaction



in aqueous dioxan is of second order over-all [1]. However the absolute values of the periods for half-exchange were very small, and the possibility that the small differences which were observed between them were dependent upon experimental error could not be excluded. The influence of the change of concentration of each component on the rate of the reaction was not studied. The values of $\tau_{1/2}$ in Table 1 are taken from the earlier paper [1].

TABLE 1

$\text{C}_{\text{Hg}^*\text{Br}_2} = \text{C}_{\text{Hg-ester}}$	0.02	0.03	0.04
$\tau_{1/2}$, min	41	36	26

For reasons set forth above, the reaction was studied a second time. Numerous measurements showed that it is exceptionally difficult to prepare similar solutions in dioxan which would give duplicable values of the rate of isotopic exchange. In addition, the dioxan, especially when mixed with water, changed on standing, so that the rate of exchange in solutions made from these aged solvents increased. Therefore, great care was required in evaluating comparable results. The entire series of experiments of this report which are directly compared was carried out in

a rather short period (about 10 days) with one and the same portion of dioxan. The measurements were made by the method of paper radiochromatography described earlier by us [2]. The kinetics of the reaction were measured over the concentration interval 0.01-0.04 M at 60, 65, and 70°. In all cases a much longer period for the half-exchange was observed for the reaction (approximately 10 times longer) than was observed in the cited work [1], which guaranteed a greater sensitivity for the measurements.*

EXPERIMENTAL

Dioxan was purified by boiling with hydrochloric acid, followed by treatment with sodium hydroxide, and with metallic sodium, according to the methods of [3]. After distillation, the dioxan was diluted with distilled water (70% dioxane and 30% water by volume). The reaction was carried out, the test samples were removed, and the activity was measured in a completely analogous manner to that described in the preceding communication [4]. The experimental data on the change with time of the percent of exchange obtained for different but equimolecular ratios of the components at a temperature of 70° are given in Table 2. From the graph with coordinates $-\log(1-F)$, t

* Apparently this also shows a greater purity of the dioxan used in the present work, since its storage, which is accompanied by an increase of the quantity of impurities, leads to an acceleration of the reaction.

TABLE 2

$c_{\text{Hg}^* \text{Br}_2}$, M/liter	$c_{\text{Hg-ester}}$, M/liter	t , min	A_{HgBr_2} , counts/min	$A_{\text{Hg-ester}}$, counts/min	F , %	$\tau_{1/2}$, min	$K_1 \cdot 10^3$, min^{-1}
0,01	0,01	55	774	47	11,5	315	1,10
			676	40	11,2		
		130	566	74	23,2		
			523	81	26,8		
		160	518	98	31,8		
			506	119	33,3		
0,02	0,02	210	641	139	35,7	260	1,32
			591	141	38,5		
		280	659	181	43,1		
			693	210	46,5		
		130	755	129	29,2		
			846	143	28,9		
		190	932	250	42,3		
			893	217	39,1		
0,03	0,03	220	858	222	41,0	240	1,44
			596	156	40,5		
		270	815	290	52,5		
			734	259	52,1		
		310	793	343	60,4		
			911	354	56,0		
		420	824	423	67,9		
			697	368	69,1		
0,04	0,04	30	1622	56	6,7	275	1,26
		60	1664	150	16,5		
		130	1143	202	30,1		
		160	1115	264	38,3		
		200	1390	401	44,8		
		240	1344	411	46,8		
			1203	426	52,3		
		20	2256	77	6,6		
		100	2520	315	22,2		
		140	1740	303	29,6		
		180	2222	499	36,8		
		230	2046	574	44,0		

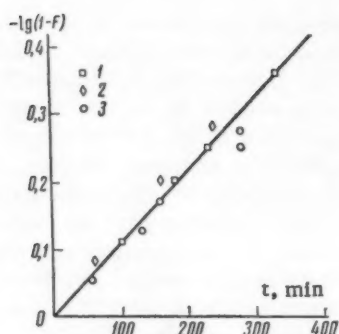


Fig. 1. The kinetics of the isotopic exchange of $\text{C}_6\text{H}_5\text{CH}(\text{HgBr})\text{COOC}_2\text{H}_5$ with $\text{Hg}^* \text{Br}_2$ in aqueous dioxan at 70° for different but equimolecular concentrations. The designations are: 1) 0.04; 2) 0.03; 3) 0.01 M. The straight line is drawn only for $c = 0.04$.

TABLE 3

$c_{\text{Hg}^* \text{Br}_2}$, M/liter	$c_{\text{Hg-ester}}$, M/liter	$\tau_{1/2}$, min
0,01	0,04	60
0,04	0,01	~600
C	C	~300

TABLE 4

$c_{\text{Hg}^* \text{Br}_2}$, M/liter	$c_{\text{Hg-ester}}$, M/liter	$\tau_{1/2}$, min	$K_1 \cdot 10^3$, min^{-1}	$K_2 \cdot 10^3$, liters/M-min
0,03	0,02	234	1,21	4,03
0,03	0,03	405	1,44	4,82
0,03	0,04	210	1,41	4,71
0,02	0,03	186	1,49	7,45
0,04	0,04	275	1,26	3,16
0,02	0,02	260	1,32	6,68
0,04	0,03	310	1,28	3,20

(Fig. 1), one can find the average value of the time for half-exchange. As is clear, the time for half-exchange for the case when $c_{\text{HgBr}_2} = c_{\text{Hg-ester}}$ does not depend on the concentrations, and within the limits of error remains constant. It follows first of all from this that the reaction is not bimolecular.

Let us analyze the equation for the kinetics of the isotopic exchange

$$Rt = -\frac{\ln(1-F)}{A+B} AB \quad (1)$$

for the assumptions that the reaction is of first order in component A and of zero order in component B.

$$R = k \cdot A$$

Then equation (1) then takes the form

$$Rt = -\frac{\ln(1-F)}{A+B} B^* \quad (2)$$

The relation for the time of half-exchange, $\tau_{1/2}$, follows from this

$$\tau_{1/2} = \frac{\ln 2}{k} \cdot \frac{B}{A+B} \quad (3)$$

From formula (3) it is apparent that the components A and B are not equally effective, and that a change of concentration of either for a constant concentration of the other must have a different influence on the magnitude of the period of half exchange. Let us construct the following two graphs:

$$\begin{aligned} \tau_{1/2} &= f(A), B = \text{const (Fig. 2) and} \\ \tau_{1/2} &= f(B), A = \text{const (Fig. 3)} \end{aligned}$$

$$\lim_{A \rightarrow 0} \tau_{1/2} = \frac{\ln 2}{k} \quad \lim_{B \rightarrow 0} \tau_{1/2} = 0$$

$$A \rightarrow 0 \quad B \rightarrow 0$$

$$B = \text{const} \quad A = \text{const}$$

$$\lim_{A \rightarrow \infty} \tau_{1/2} = 0 \quad \lim_{B \rightarrow \infty} \tau_{1/2} = \frac{\ln 2}{k}$$

$$\begin{aligned} A &\rightarrow \infty & B &\rightarrow \infty \\ B &= \text{const} & A &= \text{const} \end{aligned}$$

From Figs. 2 and 3 it is clear that if the concentration of the component for which the reaction is first order (A), is maintained constant, then an increase of the concentration of the component for which the reaction is of zero order (B) will lead to its deceleration (Fig. 3 - an increase of $\tau_{1/2}$), and a decrease of its concentration to an acceleration of the reaction (a decrease of $\tau_{1/2}$). This peculiarity may be used as the basis of a method for the determination of the order of a reaction for each of the components in the general case of monomolecularity, if the order for one of the components is zero. The corresponding experimental data are presented in Table 3.

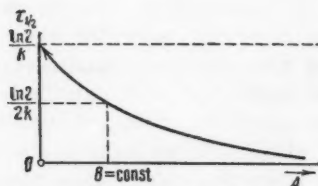


Fig. 2. The dependence of $\tau_{1/2}$ on A for a constant concentration of B in agreement with formula (3).

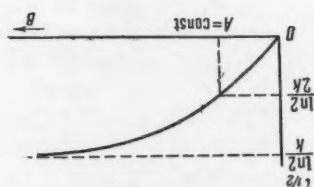


Fig. 3. The dependence of $\tau_{1/2}$ on B for a constant concentration of A in agreement with formula (3).

TABLE 5.

$c_{\text{HgBr}_2} = c_{\text{Hg-ester}}, \text{M/L}$	Temp. °C	t, min	$A_{\text{HgBr}_2}, \text{counts per min}$	$A_{\text{Hg-ester}}, \text{counts per min}$	F, %	$\tau_{1/2}, \text{min}$	$K_1 \cdot 10^3, \text{min}^{-1}$
0,04	70	35	1749	119	12,7	190	1,82
		70	1932	213	19,9		
		110	1711	330	32,4		
		140	1376	348	40,3		
		170	1297	415	48,5		
0,04	65	220	1752	624	52,5	320	1,08
		90	1216	127	18,9		
		150	1209	205	29,0		
		250	1284	329	40,8		
		350	1257	443	52,1		
0,04	60	450	1457	729	66,6	620	0,56
		100	1847	117	11,9		
		200	1659	225	23,9		
		300	2110	361	29,2		
		400	2228	346	26,9		
0,02	60	400	1622	372	37,3	620	0,56
		100	1957	419	35,4		
		200	1021	61	11,2		
		300	1118	107	17,5		
		400	1131	130	20,6		
			905	152	28,8		
			1093	166	26,4		
			956	205	35,4		
			1017	231	37,1		

Note: Data were obtained at 60° for two concentrations: $c = 0,04$ and $0,02$, which visually showed the independence of the rate of exchange on the concentration. This is the basis on which the time of half-exchange was calculated from the general curve.

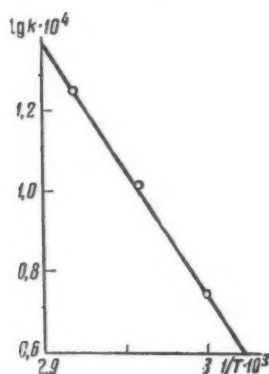


Fig. 4. The graph for the determination of the activation energy of the reaction of isotopic exchange between $\text{C}_6\text{H}_5\text{CH}(\text{HgBr}) \cdot \text{COOC}_2\text{H}_5$ and Hg^*Br_2 in aqueous dioxan solution.

TABLE 6

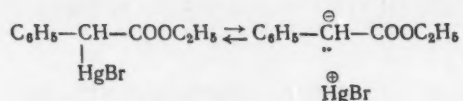
T, °K	$1/T \cdot 10^3$	$K_1 \cdot 10^4, \text{min}^{-1}$	$\lg(K_1 \cdot 10^4)$
333	3,00	5,6	0,75
338	2,96	10,8	1,03
343	2,92	18,2	1,26

From this data one can calculate that the reaction is of first order in the organomercury compound (A in formula 2) and of zero order in mercuric bromide (B in formula 2); this is confirmed by the data of Table 4, where the reaction was carried with variation of the concentration of each of the components. The calculated values of the second order constants are also presented for comparison; a large scatter was observed in these. The average value of the monomolecular constant was calculated according to formula (2), $K_1 = (1,26 \pm 0,10) \cdot 10^{-3} \text{ min}^{-1}$ at 70°. The determination of the activation energy was carried out with another portion of dioxan, the reaction in this case proceeding with a greater rate. The experimental data on the rate of the isotopic exchange at tem-

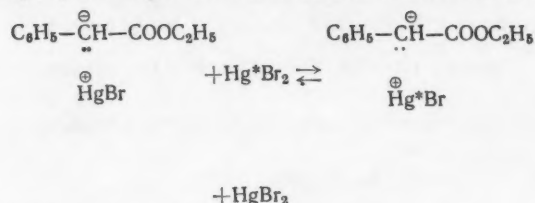
peratures of 60, 65, and 70° are presented in Table 5. In Table 6 are given the values of the first order constants, their logarithms, the absolute temperatures, and the reciprocal magnitudes of the latter. On the basis of this data the graph of the dependence of $\log K = f(1/T)$ (Fig. 4) was constructed, from which were found the parameters of the Arrhenius equation: $E = 26,7 \pm 2,1 \text{ kcal/M}$; $\log A = 14,3$. The entropy of activation $\Delta S = +6,6$ entropy units at

60°. In earlier work [1], the activation energy was found equal to 29.8 kcal/M, which, with consideration of the experimental error, agrees well with the values found by us.

The kinetic data allow us to suggest that the slowest step of the process is the ionization of the organomercury compound at the C-H bond with the formation of an internally ionized pair [6] (mechanism S_E1):



In the second step this ionized pair rapidly exchanges with the molecules of mercuric bromide:



Thus, for the first time we have established a case of a reaction of type S_E1.

SUMMARY

1. The kinetics of the reaction of isotopic exchange between the ethyl ester of α-bromomercuriphenylacetic acid and mercuric bromide labeled with Hg²⁰³ were studied in 70% aqueous dioxan solution. The parameters of the equation of Arrhenius and the entropy of activation were determined.

2. For the first time a case of an S_E1 mechanism of electrophilic substitution at a saturated carbon atom was established.

3. The kinetic equation of isotopic exchange for the case of a monomolecular reaction was analyzed. A method was suggested for the determination of the kinetic functionality of the components for a monomolecular isotopic exchange: the determination of the time of half-exchange for a large excess of one of the components.

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A STUDY OF THE TAUTOMERISM AND GEOMETRIC ISOMERISM OF NITROGEN-CONTAINING DERIVATIVES OF CARBONYL COMPOUNDS

COMMUNICATION 4. A POLAROGRAPHIC STUDY OF THE CONVERSION OF SOME SEMI- AND THIOSEMICARBAZONES IN AQUEOUS-ALCOHOLIC SOLUTIONS

Yu. P. Kitaev, G. K. Budnikov, and A. E. Arbuzov

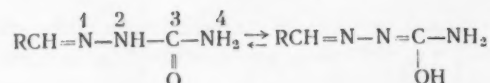
The A. E. Arbuzov Chemical Institute, Kazan Branch of the Academy of Sciences
of the USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk*,
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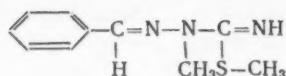
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The important and interesting question of the structure of the semi- and thiosemicarbazones has been discussed many times in the literature, mainly on the basis of the results of studies of their spectra.

The displacement of the absorption maxima of the ultraviolet spectra of the semi- and thiosemicarbazones in the long wavelength region as compared to their positions in the corresponding spectra of the carbonyl compounds is ordinarily attributed to an enolization of the urea group; this displacement has approximately the same magnitude as that induced by the introduction of a carbon to carbon double-bond $>C=C<$ into a molecule of a carbonyl group.

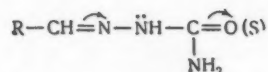


However, in the opinion of Bohlman [1] this suggestion is in error, since in the spectra of the N-methylated semi-carbazones, which are not able to enolize, a similar displacement of the maxima is observed. This author found that a further methylation of the 2-N-methylthiosemicarbazone of benzaldehyde with the formation of the following structure



had practically no influence on the absorption maximum.

The displacement of the absorption maxima in the ultraviolet spectra of the semi- and thiosemicarbazones in comparison with their positions in the spectra of the carbonyl compounds may be explained with the help of the generalized theory of conjugation [2-5]. If Bohlman [1], in giving this explanation to displacement, was considering only the influence of the free pair of electrons of the nitrogen atom neighboring the azomethine bond, then we consider that in the molecules studied by him, the semi- and thiosemicarbazones have a $\pi p\pi$ conjugated system.



This system, thanks to the presence in the conjugated chain of the N and O or S atoms is polarized, and in the mobility of the electron cloud is quite similar to the $\pi\pi$ -conjugated system; the analogy between the absorption spectra of the semi- and thiosemicarbazones and of the α, β -unsaturated carbonyl compounds also depends on this. Methylation of the nitrogen of these compounds does not substantially change the electronic structure of the molecule, and therefore there is no noticeable effect on the spectra.

On the basis of a spectrophotometric investigation of some substituted thiosemicarbazones (p-acetaminobenzylthiosemicarbazones), the suggestion was made that the $S=C$ group can play a substantial role in the formation of the electronic structure of the thiosemicarbazones [6] and an analogous influence must be shown by the $O=C$ group of the semicarbazones. A study of the infrared spectra of some thiosemicarbazones carried out by Postovskii and Shein-ker [7], showed that in the crystalline condition there is no SH group in the molecules of these compounds. This conclusion relates to the substances as they are found in the absence of reaction; however in the reaction process there can occur this or some other change of structure of the molecule.

The possibility of a conversion of the thiosemicarbazones into the thiol form upon solution in alkali was also suggested. From the fact that N^2 -methyl-substituted thiosemicarbazones are not soluble in alkali the conclusion was drawn that in the transformation of the thion group ($C=S$) into the thiol ($-C-SH$) the hydrogen atom of this nitrogen atom takes part and not the hydrogen atom on N^4 [7]. Spinks [8] suggested that under the action of ultraviolet light one might produce the thiol form of the thiosemicarbazone in which the hydrogen atoms on either N^2 or N^4 take part.

In our preceeding brief communications [9-10] we reported on the first results of a polarographic study of some semi- and thiosemicarbazones, and on the basis of these results a suggestion was made of the cause of the considerable decrease of physiological activity of the thiosemicarbazones of the aliphatic and alicyclic series in comparison with the derivatives of the aromatic aldehydes. An investigation of the behavior of semi- and thiosemicarbazones of fatty-aromatic ketones which we carried out at the dropping mercury electrode showed that in the process of irreversible reduction two electrons took part [11].

The present work is devoted to an elucidation of the connection between the polarographic data and the structure of the molecules of the semi- and thiosemicarbazones of fatty-aromatic ketones. The semi- and thiosemicarbazones of acetophenone, p-chloroacetophenone, and p-aminoacetophenone, and the semicarbazone of benzophenone were investigated. The polarographic data which we obtained shows a great similarity of behavior for the semi- and thiosemicarbazones at the dropping mercury electrode. In order to understand the influence of substituents in the benzene ring, and also the influence of the oxygen and sulfur atoms on the reducibility of these compounds, we determined exact values of their half-wave potentials under identical polarographic conditions (concentration $3 \cdot 10^{-4}$ M; pH 5.94; 3% methanol); these values are presented in Table 1.

TABLE 1

Compound	Values of $E_{1/2}$ at pH 5.94
The semicarbazone of acetophenone	1.220
The thiosemicarbazone of acetophenone	1.154
The semicarbazone of p-chloroacetophenone	1.160
The thiosemicarbazone of p-chloroacetophenone	1.112
The semicarbazone of p-aminoacetophenone	1.178
The thiosemicarbazone of p-aminoacetophenone	1.140
The semicarbazone of benzophenone	1.064

As is apparent from the polarographic data, the semicarbazones are reduced at somewhat more negative potentials than the corresponding sulfur analogs. This can obviously be explained as due to the influence of the electronegative oxygen atom on the electron density of the azomethine group, since in the case of the thiosemicarbazones, this influence by the sulfur atom is somewhat smaller. The electron-donating amino group or the chlorine atom in the para-position to the $C=N$ bond causes a displacement of the electron density in the system of π -bonds of the benzene nucleus toward the azomethine group, which leads to a concordant action of these substituents and of the electronegative atom at the ends of the conjugated system. As a result of this, the reduction of the p-chloro- or amino-substituted compounds occurs at less negative potentials as compared to the reduction of the unsubstituted compounds.

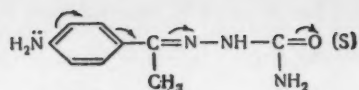


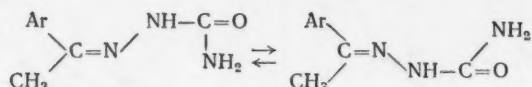
TABLE 2

Compound	The number of the polarogram	Period the solution was kept, hr	The time the solution was irradiated, hr	The characteristics of the waves			
				wave I		wave II	
				$-E_{1/2}, \text{v}$	$i, \mu\text{A}$	$-E_{1/2}, \text{v}$	$i, \mu\text{A}$
The semicarbazone of acetophenone	1	0	—	1.32	2.03	1.02	0.77
	2	24	—	1.32	1.86	1.02	1.13
	3	49	—	1.32	2.03	1.02	1.98
	4	120	—	1.32	1.80	1.02	1.28
	5	126	6	1.32	1.43	1.03	1.80
The thiosemicarbazone of acetophenone	1	0	—	1.20	5.51	—	—
	2	48	—	1.20	5.51	—	—
The semicarbazone of p-chloroacetophenone	1	0	—	1.25	1.73	1.03	0.60
	2	24	—	1.25	1.58	1.02	0.75
	3	57	9	1.26	1.63	1.01	0.79
The thiosemicarbazone of p-chloroacetophenone	1	0	—	1.16	1.46	—	—
	2	18	—	1.17	1.24	—	—
	3	23	5	—	—	1.03	1.18
The semicarbazone p-aminoacetophenone	1	0	—	1.30	3.94	—	—
	2	18	—	1.30	3.94	—	—
	3	26	8	1.30	1.24	—	—
The thiosemicarbazone of p-aminoacetophenone	1	0	—	1.24	7.09	—	—
	2	42	—	1.24	6.75	—	—
	3	50	8	1.24	5.50	—	—
The semicarbazone of benzophenone	1	0	—	1.17	5.51	—	—
	2	42	—	1.17	4.96	—	—
	3	50	8	1.17	4.28	—	—

The polarographic study showed that in aqueous-methanolic weakly acidic and neutral solutions the semi- and thiosemicarbazones mentioned, generally exist in a single form. In some cases, when these compounds were dissolved in the presence of light two waves appeared on the polarograms, the one with a more positive $E_{1/2}$ somewhat increased in proportion to the time that the solution was left standing in the presence of light. When such solutions were irradiated with ultraviolet light a further increase in the height of this wave was observed. The numerical characteristics of the polarograms are given in Table 2.

The appearance on the polarogram of a second wave and its increase in height as the solution stands in the presence of light or when it is irradiated with ultraviolet light, occurs as a consequence of the formation of a labile stereoisomer. In Fig. 1 are shown polarograms of solutions of the semicarbazone of acetophenone at pH 7.0 (the solutions did not contain agar-agar).

The formation of a stereoisomeric pair for the derivatives of the fatty-aromatic ketones apparently occurs according to the following scheme:



In the present work we did not study the stereoisomeric transition. We have touched upon this fact only in order to explain the appearance of a second wave with a more positive $E_{1/2}$. At the present time we are engaged in more detailed study of the stereoisomerism of the semi- and thiosemicarbazones.

TABLE 3.

Compound	Characteristics of the waves			
	wave I		wave II	
	$-E_{1/2}, \text{v}$	$i, \mu\text{A}$	$-E_{1/2}, \text{v}$	$i, \mu\text{A}$
The semicarbazone of acetophenone	1.15	1.50	—	—
The thiosemicarbazone of acetophenone	1.22	1.05	1.56	0.26
The semicarbazone of p-chloroacetophenone	1.15	0.97	1.54	0.24
The thiosemicarbazone of p-chloroacetophenone	1.10	0.79	1.50	0.13

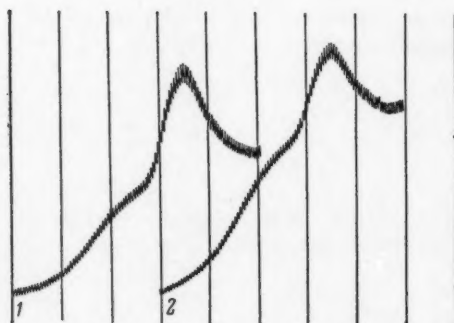
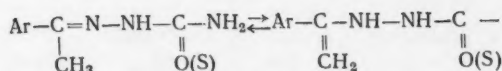


Fig. 1. Polarograms of solutions of the semicarbazone of acetophenone. The beginning of the curves -0.7 v . 200 mv/abscissa ; $S = 1/20$; 1) 120 hr after preparation; 2) after 6 hr irradiation of this solution.

When the derivatives of acetophenone and p-chloroacetophenone were dissolved in 20% aqueous methanol at pH 9.3, the polarograms of these compounds showed two waves. The characteristics of these waves are given in Table 3.

The first spread-out wave (Fig. 2) corresponds obviously to a mixture of the isomers for which the difference in $E_{1/2}$ in a weakly basic medium is clearly smaller than in a neutral solution; the polarography of such solutions gives spread-out waves. The second wave, like the first, has diffusion character as is shown by the dependence of the height of the wave on the square root of the height of the mercury reservoir; this dependence is shown in Fig. 3. The probable cause of the appearance of a second wave in the potential region about -1.5 v is the tautomeric transformation.



The enol forms of the semi- and thiosemicarbazone structures have a more basic character than the carbonyl, therefore one would expect that the first of these structures should appear in the polarograms of weakly acidic solutions. However we didn't observe this. Apparently, the deep minimum in the polarograms of solutions at pH 5.8-7.0 strongly distorts the polarographic curve and masks the second wave.

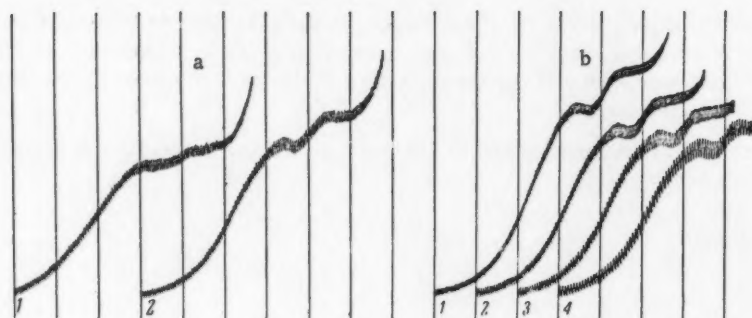


Fig. 2. Polarograms of solutions of the derivatives of p-chloroacetophenone; pH 9.3; $S = 1/7$; 200 mv/abscissa; the beginning of the curves -0.7 v. a) 1) Thiosemicarbazone; 2) semicarbazone; b) The dependence on the height of the reservoir for the semicarbazone of p-chloroacetophenone: 1) 64 cm (reduced); 2) 49 cm; 3) 42 cm; 4) 36 cm.

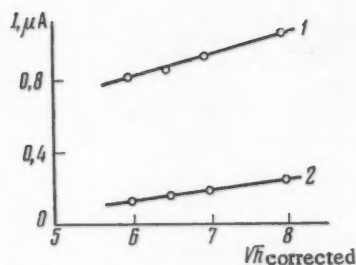


Fig. 3. The dependence of the height of the wave on the height of the mercury reservoir for a solution of the semicarbazone of p-chloroacetophenone at pH 9.3: 1) First wave; 2) second wave.

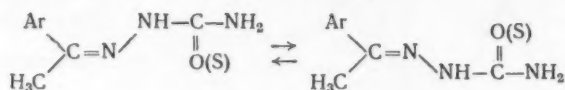
EXPERIMENTAL

A study was carried out at 20° of the changes that occur during the standing of the compounds in 20% aqueous-methanol solutions at a molar concentration of approximately 10^{-4} . The apparatus used in the work, the substances, and the solutions were described in the preceding communication [11].

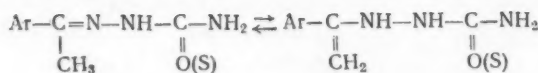
SUMMARY

1. The influence of the structure of the semi- and thiosemicarbazones on their reducibility is explained from the point of view of the contemporary representation of the structure of these organic compounds.

2. The semi- and thiosemicarbazones of fatty-aromatic compounds in weakly-acidic and neutral methanol solutions exist in a single form, which can transform to a stereoisomeric pair through the action of light.



3. In weakly basic solutions of the derivatives of the fatty-aromatic ketones two waves are generally observed on the polarogram; the most probable cause of this is the formation of two tautomeric forms.



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THE INFLUENCE OF GAMMA-RADIATION ON THE CATALYTIC ACTIVITY OF PLATINIZED ALUMINUM SILICATE

Kh. M. Minachev, M. A. Markov, and Yu. S. Khodakov

The N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

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Experimental and theoretical investigations completed during recent years on the influence of nuclear radiation on solids have definitely shown changes in the properties of solid bodies under the action of radiation. Very often irradiation leads to an increase of the specific magnetic susceptibility, to a change of electrical resistance, to a decrease of density, and to other changes in the physical properties of solid bodies.

There are a series of works in the literature on the study of the influence of nuclear radiation on heterogeneous catalysts [1-12]. In the majority of the works the authors have noted a change of catalytic activity of the catalyst after irradiation. Thus in the report [2], which is devoted to an investigation of the influence of gamma-radiation on the catalytic activity of aluminum oxide in the reaction of deuterium-hydrogen exchange, Taylor and Kohn have observed a considerable increase in the activity of the catalyst after radiation. Weiss and Schweigler [8] have observed that after irradiation of an inert silica gel with a stream of neutrons, the latter acquires activity for the cracking of isopropylbenzene and for the isomerization of hexane. Clarke and Gibson [4] studied the influence of gamma-radiation on the catalytic activity of catalysts for the Fischer-Tropsch process. It was shown that in the case of unreduced iron catalysts, the catalytic activity of the irradiated samples was 10-60% higher than the unirradiated, the increased activity being maintained during 50-300 hr of testing.

In the present work we have set for ourselves the problem of explaining the change of catalytic activity of aluminum silicate which contains 0.5% platinum for the decomposition reaction of hydrogen peroxide and for the hydrogenation of cyclohexene as it depends on the irradiation dose previously received.

EXPERIMENTAL

Commercial aluminum silicate [13] in the form of small spheres was washed free of oxides of iron and used as a carrier for the preparation of the catalyst. The prepared aluminum silicate was impregnated with the calculated quantity of a solution of chloroplatinic acid. The catalyst was reduced in a stream of electrolytic hydrogen at a temperature of 330° during 10 hr, and had a surface area (by benzene adsorption) of 252.2 m²/g [14].

Samples of the catalyst were irradiated in sealed glass ampoules which contained nitrogen gas. The energy of the gamma quanta in all cases was equal to 0.6 mev. The following radiation doses were selected: 1) $0.27 \cdot 10^{19}$ ev/g; 2) $56.15 \cdot 10^{19}$ ev/g; 3) $124.2 \cdot 10^{19}$ ev/g; 4) $279.2 \cdot 10^{19}$ ev/g; 5) $60 \cdot 10^{19}$ ev/g. The elapsed time from the irradiation to the determination of the activity was 6 months for samples 1-4, and 6 days for sample 5. The studies of the decomposition of hydrogen peroxide were made with 0.70 g of catalyst and 8.5 ml of 5.30% hydrogen peroxide.

The hydrogenation of cyclohexene was carried out in 10 ml of 99.6% ethyl alcohol, containing 1.40 g of catalyst and 0.40 g of the hydrocarbon.

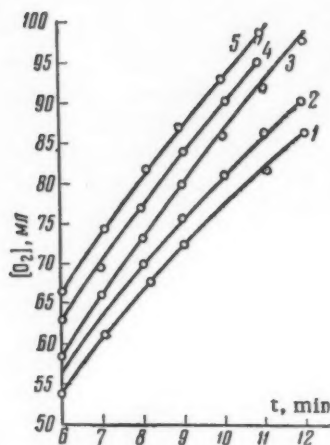


Fig. 1. The decomposition curves of hydrogen peroxide over catalysts with different radiation doses as indicated: 1) Original material and sample irradiated with $0.27 \cdot 10^{19}$ ev/g; 2) $56.15 \cdot 10^{19}$ ev/g; 3) $124.2 \cdot 10^{19}$ ev/g; 4) $279.2 \cdot 10^{19}$ ev/g; 5) $60 \cdot 10^{19}$ ev/g.

Characterization of the cyclohexene gave the following constants: $m, p = 82.5^\circ$; $n_D^{20} 1.4460$; $d_4^{20} 0.8092$. The experiments were carried out in a shaker at 600 shakes/min.

The rate of the reaction was measured by the evolution of oxygen for the decomposition of hydrogen peroxide, and by the absorption of hydrogen for the hydrogenation of cyclohexene. Each point was taken from the average of 3 experiments. As a measure of the catalytic activity for the hydrogenation of cyclohexene we took the rate constant of the reaction, since it was experimentally shown that the rate of the reaction was well described by the zero order equation.

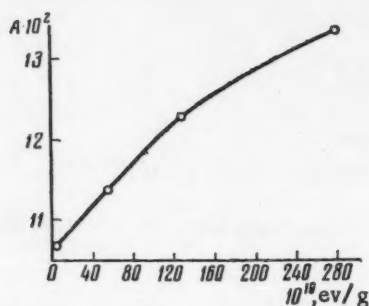


Fig. 2. The dependence between the dose of irradiation and the activity of the catalyst for the decomposition of hydrogen peroxide.

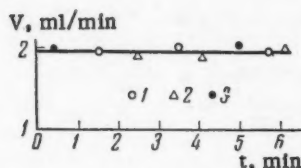


Fig. 3. The hydrogenation of cyclohexene over irradiated and unirradiated catalysts: 1) Irradiated with a dose of $60 \cdot 10^{19}$ ev/g; 2) irradiated with a dose of $279 \cdot 10^{19}$ ev/g; and 3) unirradiated catalyst.

increasing with the increase of the dose. Catalyst 5 was considerably more active than catalyst 2, notwithstanding the fact that the dose was approximately the same in both cases. These two catalyst differed only in the time that had elapsed between irradiation and the determination of the activity; for sample 5 this was 6 days, while for sample 2 this was 6 months. This reversibility of the changes arising in solid bodies under the action of irradiation agrees with the data of other authors [2, 3] who have investigated the change of properties of solid bodies under the action of radiation.

It is apparent from the data of the table that the catalyst which was irradiated with $60 \cdot 10^{19}$ ev/g had within 6 months following the radiation already lost approximately 80% of the activity which had appeared as a result of the irradiation. It should be observed that, as is apparent from Fig. 1, the activity of the catalyst irradiated with a dose of $0.27 \cdot 10^{19}$ ev/g is equal to the activity of the unirradiated catalyst. The dependence of the catalytic activity on the irradiation dose is shown in Fig. 2. From the figure it can be concluded that in the region of relatively small doses of radiation there is a direct proportionality between the irradiation dose and the catalytic activity of the investigated catalyst. In the region of large doses, the catalytic activity increases more slowly.

The Influence of the Dose of Radiation on the Catalytic Activity of a 0.5% Platinized Aluminum Silicate for the Decomposition of Hydrogen Peroxide

Irradiation dose, ev/g	Elapsed time before testing	$A = 1/\tau$
$0.27 \cdot 10^{19}$	6 months	0.1065
$56.15 \cdot 10^{19}$	6 months	0.1135
$124.2 \cdot 10^{19}$	6 months	0.1228
$279.2 \cdot 10^{19}$	6 months	0.1395
$60 \cdot 10^{19}$	6 days	0.1450

The decomposition of hydrogen peroxide over the unirradiated catalyst followed the second order equation:

$$kt = \frac{[H_2O_2]_0 - [H_2O_2]_t}{[H_2O_2]_0[H_2O_2]_t},$$

where k is the rate constant of the reaction; t is the time; $[H_2O_2]_0$ is the initial concentration of the peroxide or the concentration after time t .

However in the case of the irradiated catalyst a deviation from second order occurred, and therefore, provisionally, we took the value reciprocally proportional to the period of half-decomposition of the hydrogen peroxide $A = 1/\tau$. The experimental data obtained are presented in Figs. 1-3 and in the table.

In Fig. 1 are depicted the decomposition curves for hydrogen peroxide on unirradiated and irradiated catalysts from the 6th to the 12th minutes. It is clear from Fig. 1 that the curves for the irradiated catalyst lie higher than the curve for the unirradiated catalyst, the catalytic activity

The results obtained for the hydrogenation of cyclohexene over unirradiated and irradiated samples of catalysts are shown in Fig. 3. As is apparent from this figure, the hydrogenation curves for all samples are identical, i.e., for the hydrogenation of cyclohexene we did not observe a change of catalytic activity of the 0.5% platinumized aluminum silicate after irradiation with gamma-rays.

SUMMARY

1. The influence of gamma-radiation on the catalytic activity of platinumized aluminum silicate for the reaction of hydrogen peroxide decomposition and for the hydrogenation of cyclohexene was investigated.

2. The rate of the decomposition reaction of hydrogen peroxide grew with an increase of the irradiation dose to the catalyst.

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A PHOTOCHEMICAL STUDY OF THE MECHANISM OF THE REACTION BETWEEN OXYGEN ATOMS AND ACETALDEHYDE

L. N. Avramenko and R. V. Kolesnikova

Institute of Physical Chemistry, Academy of Sciences of the USSR

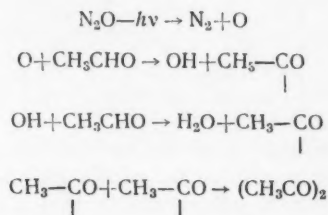
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Original article submitted August 2, 1960

Photochemical experiments have been conducted with a view to obtaining additional data relating to the reaction: $O + CH_3CHO \rightarrow$, and to the properties of the acetyl radical, at higher pressures than are used in the discharge method [1].

The reaction between oxygen atoms and acetaldehyde has been studied by the photochemical method by Tsvetanovich [2]. In his experiments, the initial oxygen atoms were provided by the decomposition of nitrous oxide photo-sensitized by mercury. In the reaction products obtained by irradiating the nitrous oxide-acetaldehyde mixture by means of a mercury lamp, have been observed diacetyl, but acetic acid was not found. Tsvetanovich proposed the following reaction scheme on the basis of his experiments:



In our experiments [1] using the discharge method, in which oxygen atoms were produced from oxygen molecules in a high potential discharge under comparatively low pressures (1-15 mm Hg), the reaction products included acetic acid, glycolic aldehyde, ketene and formaldehyde, but diacetyl was not found. Special attention has been paid in the present work to the formation of acid and of diacetyl.

EXPERIMENTAL

The apparatus used for our photochemical experiments consisted of a quartz vessel of volume 116 cm³ and diameter 2.5 cm. Illumination was provided by a mercury quartz lamp L-75 provided with a reflector. The vessel contained drops of mercury. The experiments were carried out at 30°C. The mixture of nitrous oxide and acetaldehyde was prepared in an 8 liter flask, which was carefully shielded from light. The mixture could be left for a period of months without changing its composition. The quartz vessel was connected by means of a tap and a detachable trap to a vacuum system and manometers. The mixture of nitrous oxide and acetaldehyde could be frozen out in the trap, and then heated, the pressure being measured. The mixture could be frozen out completely, giving no measurable pressure. Pure nitrous oxide, submitted to illumination from the quartz lamp and then to freezing out, gave a residual pressure due to nitrogen and oxygen. From this residual pressure it was possible, knowing the volume, to calculate the extent of the photochemical decomposition of the nitrous oxide. It was shown in this way that when $P_{N_2O} = 200$ mm and irradiation is carried out for a period of 1 hr, the number of molecules of nitrous oxide decomposed was $3.6 \cdot 10^{18}$.

By submitting the nitrous oxide - acetaldehyde mixture to irradiation, and subsequently collecting both the initial products and the reaction products in the trap, it was possible to determine the quantity of reaction products. Amongst the reaction products both acetic acid and diacetyl were tested for. About 2 ml of water or alcohol were previously placed in the trap; water was used in analysis for the acid, and alcohol in analysis for diacetyl. Analysis

for diacetyl was performed by means of the well-known reaction in which it is converted into nickel dioxime. For precipitation dry hydroxylamine hydrochloride, a dilute solution of a nickel salt, and 0.1 N sodium hydroxide were used. Preliminary experiments were carried out with pure diacetyl at the same low concentrations which could be expected in the reaction. Using diacetyl in a quantity of $2.8 \cdot 10^{-6}$ M we obtained a good precipitate of nickel dioxime. Half this concentration represented the practical limit of the method.

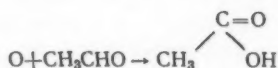
Since it is known that under the influence of excited mercury, not only nitrous oxide but also acetaldehyde is decomposed, the mixtures were initially made up with only low acetaldehyde concentrations, so that as far as possible the acetaldehyde should not be destroyed by the excited mercury. Afterwards mixtures with larger acetaldehyde concentrations were made up. Measurements by other authors [3] show that the destructive action of acetaldehyde with respect to excited mercury is about twice as great as that of nitrous oxide. Experiments were therefore carried out with various compositions of the initial gases, and at different pressures. The experimental results are shown in the table.

Expt. No.	Composition of mixture	Pressure, mm Hg	Illumination time, hours	Reaction products	
				quantity of acid	quantity of diacetyl
1	$\frac{\text{CH}_3\text{CHO}}{\text{N}_2\text{O}} = \frac{4.5}{100}$	From 50 to 428	1	Not found	Not found
2	$\frac{\text{CH}_3\text{CHO}}{\text{N}_2\text{O}} = \frac{1}{2}$	432	1	$3 \cdot 10^{-6}$ M	" "
3	The same	432	3	$6 \cdot 10^{-6}$ M	" "
4	" "	50	3	Not found	" "
5	" "	450 of reagents + + 400 Argon	3	" "	" "
6	" "	450 of reagents, 400 of CO ₂	3	" "	" "

As we can see from the table, a mixture of nitrous oxide and acetaldehyde containing 4.5% acetaldehyde, illuminated for 1 hr at pressures varying from 50 to 428 mm Hg, gives neither diacetyl nor acid. In a mixture with ratio of acetaldehyde to nitrous oxide of 1:2, acid capable of titration with alkali is produced in notable quantities. Increase in pressure of the mixture produces increase in the acid yield.

In order to solve the question as to whether this increase in acid yield is due to increase in pressure only, or to increase in the acetaldehyde concentration, experiments 5 and 6 were undertaken. The table shows that dilution of the mixture with argon or carbon dioxide leads to no rise in the yield of acid. From this it may be concluded that the third particle plays no part in the formation of acid from the atoms of oxygen and the acetaldehyde. The experiments show that the ratio of acetaldehyde to nitrous oxide affects the yield of acid from the reaction $\text{O} + \text{CH}_3\text{CHO} \rightarrow$ (see, for example, experiments 1 and 2). It is found that the acid yield is low in mixtures containing a low acetaldehyde content, and increases with increase in this quantity. This fact may be explained if it is supposed that, in the presence of low acetaldehyde concentrations, a portion of the oxygen atoms reacts with the nitrous oxide, leaving fewer capable of reaction with the acetaldehyde. The greater the value of the acetaldehyde concentration, the greater the proportion of oxygen atoms entering into reaction with the acetaldehyde. Thus a description of the mechanism of the interaction between oxygen atoms and acetaldehyde must take into account two facts: (1) the formation of acetic acid, and (2) the absence of any formation of diacetyl.

Just as in the previous work [1], we come to the conclusion that the oxygen atoms attack the acetaldehyde at the C-H bond, thus:

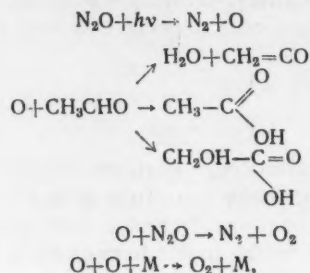


The absence of diacetyl may be explained in two possible ways: Either acetyl radicals are not formed in the reaction, or they are removed preferentially by disproportionation, forming acetaldehyde and ketene.

It is evident from our own experiments that, using the discharge method, the reaction of hydrogen atoms with acetaldehyde at low pressures (3-15 mm Hg) produces acetyl radicals, which then produce ketene and so lead to the

formation of acetic acid, and which do not form diacetyl. It is important that this property of the acetyl radicals should be confirmed for pressures of the order of atmospheric. We have therefore carried out photochemical experiments at such pressures. In these experiments the quartz vessel containing mercury drops was supplied with an acetaldehyde hydrogen mixture at 600 mm Hg in which $(\text{CH}_3\text{CHO}) : \text{H}_2 = 8,50$. After mixing, the system was illuminated with a mercury lamp for 1 hr, and analysis of the reaction products was then carried out. Acetic acid was found in quantities of the order of $5 \cdot 10^{-5}$ M, while diacetyl was not observed even in traces (i.e., less than $1,4 \cdot 10^{-6}$ M was present).

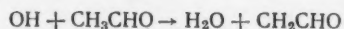
From these results the following reaction mechanism could be derived:



where M represents the third particle (nitrous oxide).

This scheme explains the phenomena observed in our experiments, and is in agreement with our other observations, showing the predominance of processes in which the oxygen atom employs both its valences. We note also this experimental fact, that both in the illumination of nitrous oxide-acetaldehyde mixtures, and in that of hydrogen-acetaldehyde mixtures, the formation of polymers is observed, deposited on the walls of the quartz vessel in the form of fine, transparent, solidified drops. It may be supposed that, in the hydrogen-acetaldehyde reaction, polymers of ketene are produced, while in the nitrous oxide-acetaldehyde reaction polymers of glycolic aldehyde arise. Additional and more reliable analysis is needed, however, before this can be regarded as established.

In conclusion, we wish to indicate a suggested mechanism for the reaction occurring during illumination of a nitrous oxide-acetaldehyde mixture containing low concentrations of acetaldehyde. In this process, together with the formation of oxygen atoms, there also occurs the formation of hydrogen atoms through interaction of acetaldehyde and mercury. These hydrogen atoms may react with the acetaldehyde, forming hydroxyl radicals: $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$. The excess of nitrous oxide favors this process. We have studied specially the interaction of hydrogen atoms with nitrous oxide, and have shown that, at 80° and 3 mm Hg, formation of hydroxyl ions does in fact occur. These radicals may then react further with acetaldehyde according to the reaction:



The CH_2CHO radicals may recombine, with the formation of succinaldehyde. Thus, for low acetaldehyde concentrations, the reaction products may be water and succinaldehyde.

SUMMARY

1. Under the conditions of photochemical experiments at pressure near atmospheric, the reaction between atomic oxygen and acetaldehyde proceeds according to the same mechanism as under the conditions of the discharge method at pressure between 1 and 15 mm Hg, and in both cases produces acetic acid.

2. Acetyl radicals, both at low pressures and at near-atmospheric pressures, are capable of undergoing disproportionation, but not recombination.

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THE ROLE OF OXYGEN IN STRUCTURE FORMATION ON METAL SURFACES

N. A. Shishakov, N. K. Andrushchenko, and U. A. Asanov

The Institute for Physical Chemistry, Academy of Sciences of the USSR

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There are examples known in mineralogy where the uniform orientation of one type of crystal on the surface of another can be explained by the similarity in structure of the faces on which growth occurs. The large number of such cases leaves no doubt as to the existence of a general law, and we might therefore refer to the same category of phenomena the oriented growth of crystals in thin films on metal surfaces. However, there are serious objections to this. A metal surface does not have the same characteristics as a mineral surface. If a metal surface is clean, then it can strongly chemisorb oxygen. The structure then alters so markedly that the conception of a similarity in structure of the metal and oxide surfaces loses any significance. Systematic study of these phenomena [1] has led to the conclusion that it is not the structure of the metal surface, but the properties of oxygen (the large size and negative charge of its ions and their tendency to dense packing on any metal facet) which determine the structure and crystal orientation of a surface oxide.* Our new investigations have enabled us to track down these phenomena in more detail.

EXPERIMENTAL

The subjects of our investigation were palladium and gold and their oxygen derivatives. Palladium oxide, PdO , having the structure shown in Fig. 1, is normally obtained by heating the metal, usually at a high oxygen pressure. We used this and another method. Palladium was evaporated from a heated wire in oxygen, and the deposit formed on a glass plate at room temperature was investigated by electron diffraction. At very low oxygen pressures the product was practically pure palladium (Fig. 2), but, with about 0.1 mm Hg pressure of oxygen, the condensed layer showed no metallic sheen and electron diffraction photographs only revealed palladium oxide reflections (Fig. 3 and Table 1). The diffraction pattern indicated that most of the oxide crystals were oriented in (001) planes, and the rest in (101) planes parallel to the surface of the glass plate. The intensity distribution calculated on this basis is shown diagrammatically in Fig. 4.

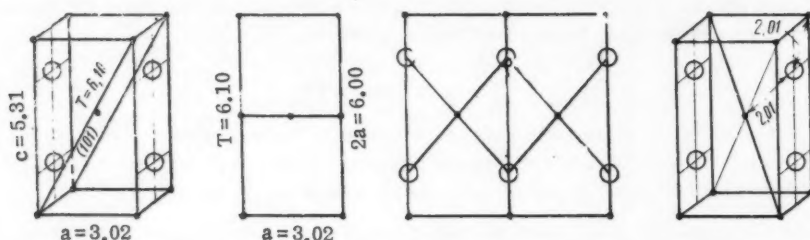


Fig. 1. The structure of palladium oxide, showing the relations between the dimensions of the cell faces.* *

The simultaneous existence of two structural axes shows that these depend on each other. This is confirmed by Fig. 1, from which it is obvious that twice the area of the base of the cell is almost exactly equal to the area of

* There are other factors in the case of thick films, such as the direction of travel of metal atoms during condensation, or the direction of lines of force during electrolysis.

* * Dimensions of figure were not clear in the Russian—Publisher's note.

TABLE 1. Analysis of the Electron Diffraction Patterns of Films Obtained by Condensation of Palladium on Glass in Oxygen at a Pressure of 0.1 mm Hg (tetragonal lattice with parameters $a = 3.02$ and $c = 1.76$ Å)

Experimental data			hkl	Theoretical data		
δ , deg.	I	d , Å		δ , deg.	d , Å	$I_{\text{theor.}}$
20	3	3.07	100	90	3.02	1
0	10	2.65	002	0	2.65	1
60	5	2.65	011	60	2.63	10
50	10	2.15	110	90	2.14	1
20	3	2.03	102	41	2.00	1
40	10	1.66	112	51	1.66	6
30 60	3	1.52	013	30	1.53	3
30	10	1.50	200	90	1.51	3
0	10	1.32	004	0	1.33	1
50	10	1.32	211	76	1.31	4
30	5	1.32	022	60	1.31	1
50	2	1.15	114	32	1.13	1
30 60	3	1.10	123	52	1.08	3
20	3	1.01	105	19	1.00	1
45	3	1.01	301, 204	79 41	0.99	2
60	3	0.91	312	70	0.90	3
0	3	0.90	006	0	0.89	0.1
60	5	0.89	303	60	0.88	1
45	5	0.84	215, 224	38 51	0.83	1
20	3	0.78	314, 026	54	0.77	1

* I is the reflection intensity; δ is the angle between the radius vector of the beam and the line of symmetry of the diffraction pattern; d is the distance between the planes; I_{theor} is the calculated intensity for a completely random crystal distribution.

TABLE 2. Analysis of the Electron Diffraction Pattern of a Palladium Surface, Condensed on Glass in Oxygen at a Pressure of 0.1 mm Hg and then Heated for 10 Hours in Air at 150° (hexagonal lattice with parameters $a = 5.44$ and $c = 6.86$ Å)

δ , deg.	I	d_{exp} , Å	hkl	d_{calc} , Å
60	10	4.00	101	3.89
0	10	3.42	002	3.43
Continuous line	10	2.86	102	2.77
60	2	2.31	200	2.29
0-15	3	2.07	103	2.06
0	5	1.71	004	1.72
Continuous line	3	1.62	104	1.61
70	2	1.54	300	1.57
0-15	3	1.45	114	1.45
0	3	1.31	105	1.32
Continuous line	2	1.13	006	1.14

the (101) face of the cell. This is not surprising, but it makes it difficult to give a clear explanation of such crystal growth. In the analogous case of platinum, sputtered in oxygen at 0.1 mm pressure, it has been shown [1, 2] that PtO_2 molecules are first formed in the vapor, and that these condense with their correct packing to give a black deposit of platinum dioxide with a hexagonal lattice. It is possible that in the case of palladium, the deposit is obtained by condensation of preformed PdO molecules with an abnormal packing. Looking at the structure in Fig. 1, we may pick out of its O-Pd-O groupings with a Pd-O separation = 2.01 Å, which can be considered as previously free molecules.

There was a marked change in the surface structure when such a product was heated in air for 10 hr at 150° (Fig. 5 and Table 2). In this case, the lattice constant along the axis normal to the glass surface was 3.4 or 6.8 Å.



Fig. 2. Electron diffraction photograph of metallic palladium.

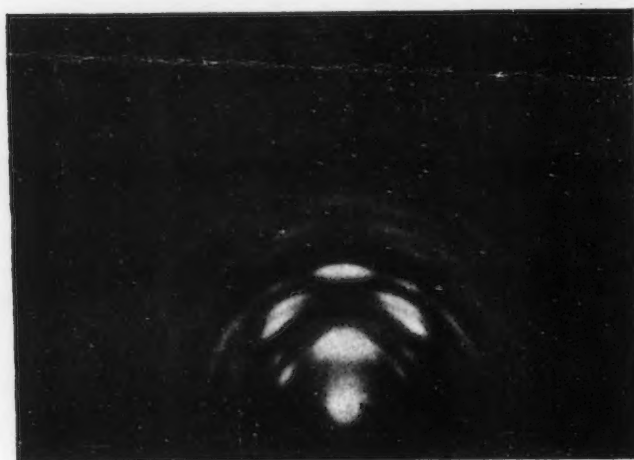


Fig. 3. Electron diffraction photograph of palladium oxide with a tetragonal lattice and two structural axes.

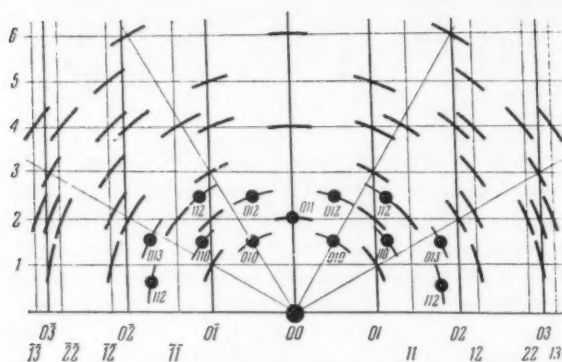


Fig. 4. Calculated beam distribution for the electron diffraction pattern of palladium oxide with two structural axes.

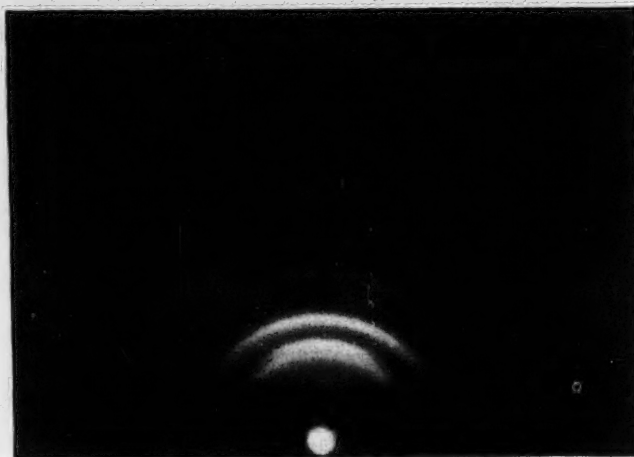


Fig. 5. Electron diffraction photograph of palladium peroxide with hexagonal lattice.



Fig. 6. Electron diffraction photograph of the surface of condensed palladium treated for a long time with oxygen at low pressure.

This shows the closeness of the structure to those of the previously described gold [1] and platinum [2] peroxides with hexagonal lattices. It must therefore also be considered possible that there exists a surface palladium peroxide.

Oxygen had a marked effect on a preformed palladium film obtained by condensation in high vacuo. In one experiment, oxygen was admitted over a 24 hr period, through a fine capillary, to a flask containing a fresh palladium film, so that the pressure in the flask remained very low throughout. The results are shown in Fig. 6, where for the first two diffuse lines, $d = 2.6$ and 1.6 Å. This shows that the oxygen caused substantial breakdown of the previous palladium lattice.

Heating of this product for 15 hr at 150° in air gave rise to crystals with a cubic face-centered lattice, with the parameter $a = 5.6$ Å (Fig. 7 and Table 3). By analogy with the previously investigated peroxides and carbonyls of platinum [3], we consider that in this case palladium peroxide had been formed with a cubic lattice, probably of the NaCl type.

Oxygen compounds of palladium are not only formed in surface films. Palladium was condensed in oxygen at 0.1-0.2 mm Hg pressure onto a cellulose film, so as to give a layer a few hundred Å thick. Fig. 8 shows that

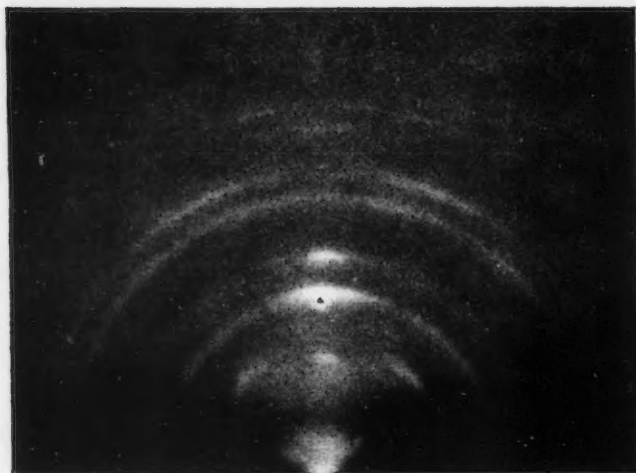


Fig. 7. Electron diffraction photograph of palladium peroxide with a cubic face-centered lattice.

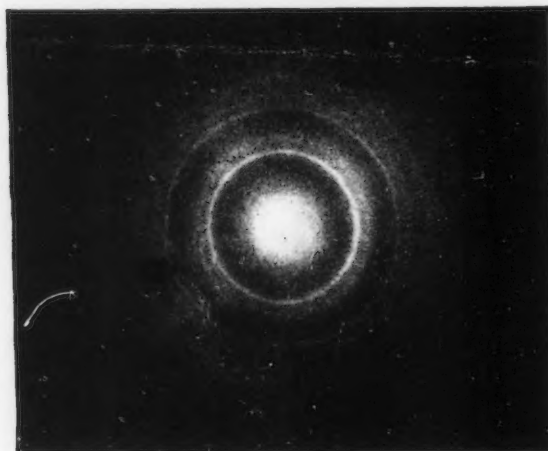


Fig. 8. Electron diffraction photograph of a thick, free palladium film, obtained by condensation in oxygen and containing a very large amount of tetragonal oxide.

this layer consisted mainly of palladium oxide (the thin lines 011, 112, 103 + 200, 121). Metallic palladium, in small amounts, was also present in the film (see second diffuse ring with indices 111).

A different phenomenon was observed with a gold surface. When gold was condensed on a thin cellulose film or on a glass plate, with an oxygen pressure of 0.1 mm, formation of oxygen compounds was also observed. However, in the first case this was made evident by the appearance of diffuse rings with $d = 3.4$ and 1.7 Å (Fig. 9), as with thin gold films heated at $100-150^\circ$ (see [1]), while in the second case a few diffuse arcs were observed (Fig. 10), also found previously when gold films on glass were heated. In this case, there was probably some formation of gold peroxide. Clearer results were obtained when deposits of clean gold on glass were heated to 250° . In a previous investigation [1] the heating was carried out for several hours in an oxygen stream, and the indications were that peroxide was formed with the molecular oxygen ions mainly oriented so that their axes were normal to the glass surface. In the present investigation, the heating was carried out for many hours, and only in air. It was found that the surface structure altered considerably in the course of time.

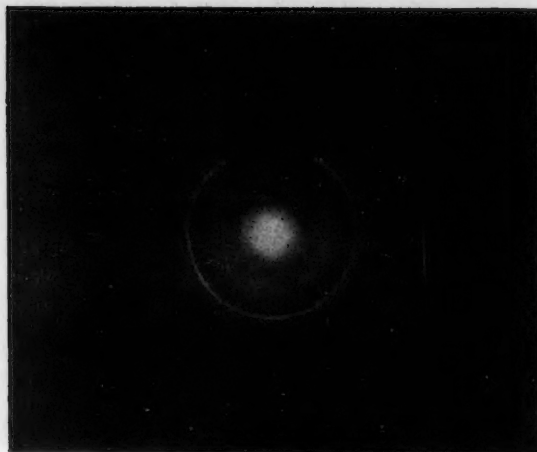


Fig. 9. Electron diffraction photograph of gold peroxide, obtained by condensation of metal in oxygen (note inner diffuse ring).

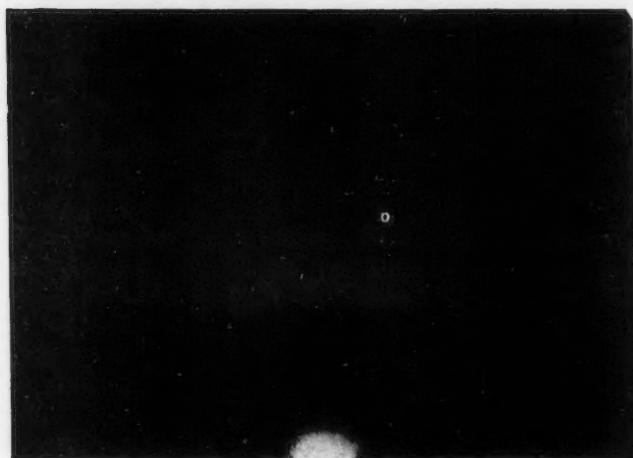


Fig. 10. Reflection of electrons from the same gold peroxide surface, scarcely noticeable in Fig. 9.

Figure 11 shows the electron diffraction photograph of a product which had been heated for 100 hr. The pattern is characterized by numerous short arcs, distributed in a complex way about the line of symmetry. This indicates the existence of several lattice constants along the axis normal to the glass plate, i.e., the presence of several surface structures. Probably these structures are genetically related to each other, as the underlying structure depends on the orientation of the structures located above, or the other way round. This gradation in passing from metal to a series of different structures of oxygen compounds, which is a general property of the surface layers of metals, is particularly well defined with gold, and has been noted by other authors [4] as well as by us.

The same glass plate with a gold film was heated at 250° for a further 100 hr. Figure 12 shows the result. Confirmation of our ideas follows from the appearance on the diffraction photograph of well defined sharp points in addition to the above mentioned short arcs; the relatively high intensity of these points shows that they are produced by the whole surface of the layer, and their sharpness indicates ideally precise orientation of the corresponding crystals. The apparent lattice constant along the normal to the surface is here 2.8 Å. A similar phenomenon has been observed previously [3] with a platinum surface which had been evaporated in carbon monoxide at 0.1 mm pressure and



Fig. 11. Electron diffraction photograph of a mixture of metallic gold and its surface peroxide, obtained from the previous sample (Fig. 10) by prolonged heating in air at 250°.



Fig. 12. Electron diffraction photograph of the previous sample (Fig. 11) after additional prolonged heating in air at 250°.

subsequently heated in air for a long time at 150°. It was found in this case that evaporation gave rise to platinum carbonyl, with a cubic lattice, and with the (001) axes of the crystals oriented normal to the surface; subsequent heating in air produced enrichment of this with molecular oxygen ions and platinum atoms, probably leading ultimately to the composition $\text{Pt}(\text{O}_2)$. It is therefore probable that in the case of gold we were dealing with a surface peroxide possessing a cubic lattice.

The short arcs on the electron diffraction photograph (Fig. 11) are attributed to different structures. The most intense of these may be assigned to 111, 002, and 222 reflections from metallic gold, since they correspond to the known lattice parameter 4.05 ± 0.05 Å. The other short arcs, with lattice constants 5.0, 4.03, 3.38, 1.69, and 1.45 Å may be attributed to other intermediate compounds.

DISCUSSION

The simultaneous occurrence in one film of two structural axes, (111) and (001), as observed in Fig. 11, is a fairly common phenomenon. It occurs, for example, in electrolytically deposited nickel, and in surface oxides of

TABLE 3. Analysis of the Electron Diffraction Pattern of Palladium Peroxide, Obtained by Heating Amorphous Palladium Oxide in Air for 15 Hr

δ , deg.	l	d , Å	hkl	a
0	5	3,21	111	5,56
50	10	2,82	200	5,64
0 & 60	10	1,98	220	5,59
30 & 60	3	1,65	311	5,48
0	5	1,62	222	5,57
50	2	1,41	400	5,64
20,45 & 60	5	1,27	331	5,59
25	5	1,16	420	5,64
0	3	0,99	440	5,60
20	5	0,93	600/442	5,58

Mean 5,60 Å

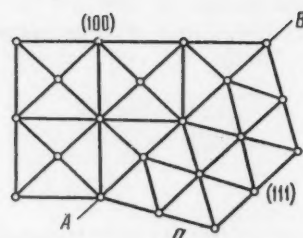


Fig. 13. Diagram explaining the recrystallization of a two-dimensional cell cubic face-centered lattice.

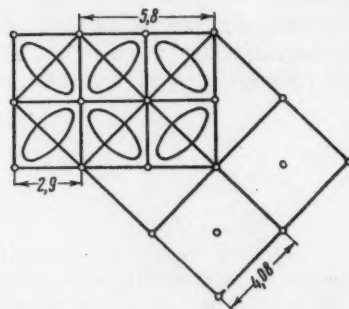


Fig. 14. Diagram explaining the fitting of a metallic gold lattice to surface peroxide with a cubic lattice.

nickel obtained by heating in air at 400° [5]. It can be explained with the aid of Fig. 13. Let us suppose that a face-centered cubic lattice is oriented with the (111) plane parallel to the plane of the diagram, and that the left hand face of the lattice shown will be (100). Clearly, with such an initial orientation and in the absence of external interference, the crystal will continue precisely with its previous form of growth, and the distance $a\sqrt{3}/2$ between the lines will be preserved. Now we may suppose that because of some accidental barrier, some of the atoms of the succeeding line to the left are more widely spaced, so that the distance between the lines will be a . This may take place to a sufficient extent so that a square atomic lattice begins to form, and with respect to this lattice the indices of the line AB will be (110). In the third dimension, both these parts of the crystal will grow with the above-described two orientations, as observed experimentally, particularly with gold. Thus, initially along the common lines and then throughout the common planes, the associated orientations will be produced in the different layers, as evidenced by Figs. 11 and 12.

We may suppose that surface gold peroxide has a characteristic cubic lattice of the sodium chloride type, but with a variable number of cations depending on the history of the product. In this case, the structural axis of the cubic gold peroxide will, as with platinum peroxide, be the (001) axis, so that the parallelism of the (001) planes of peroxide and metal to each other may be explained by the similarity in structure of the lattices as well as of the lines (Fig. 14).

However, it does not follow that such an orientation of gold crystals is the cause of a similar orientation of the peroxide. It appears more probable that the main causes of the latter are the ordered chemisorption of oxygen molecules (independent of the initial orientation of the metal crystals), the ordered diffusion of cations outwards, and the above mentioned fitting of the metal atoms underneath to the surface peroxide formed. Indeed, such a

mechanism for the formation of oxide (and peroxide) films on metals was also considered in our previous work [1], where other facts discovered by volumetric and optical investigation were used to supplement the electron diffraction studies.

SUMMARY

1. It has been established that several structural axes can exist simultaneously in surface oxide compounds of palladium and gold.

2. These genetically related orientations are determined by the closeness in structure of the atom lines, as well as by the closeness in structure of the atom planes. The main reason for the orientation of oxide on metals is the ordered adsorption of oxygen.

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THEORY OF FLAME PROPAGATION IN SYSTEMS WITH CHAIN BRANCHING REACTIONS

L. A. Lovachev

Institute of Chemical Physics, Academy of Sciences of the USSR

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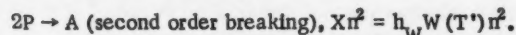
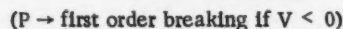
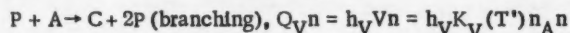
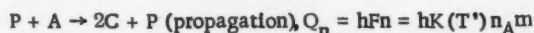
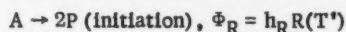
The theory of laminar flame propagation for systems with nonbranching chain reactions has been developed by the author in earlier articles [1-4] and confirmed by comparison with experimental results from chlorine-hydrogen flames [3, 4]. In the first part of the present paper a theory of flame propagation is proposed for systems with chain branching reactions represented by a model reaction with an active center of one type. This problem is solved by calculating the rate of chain propagation, the rate of chain branching and the rate of second order chain breaking. In the second part of the article a solution is proposed for flame propagation in a system with chain branching reactions including three active centers [5]. The burning of hydrogen is taken as an example of this kind of reaction. In the second part a system of equations of thermal conductivity and three equations for the diffusion of the hydroxyl group, the hydrogen atom and the oxygen atom are considered, but without taking into account second order chain breaking.

The Model Uni-center Chain Reaction

In their investigation, Giddings and Hirschfelder [6] integrated numerically a system of differential equations describing the flame propagation process occurring with a chain branching reaction which was represented by a model reaction with one active center and included two processes: $2P \rightarrow A$ (second order chain breaking) and $P + A \rightarrow C + 2P$ (the process of propagation and chain branching).

The complete solution of the problem of the propagation of a flame for the case of a unicenter model reaction was reported by the author [7], where relatively simple formulae for determining the flame propagation velocity, taking into account the effect of chain branching and second order chain breaking, were derived for a reaction of the type degenerating-branched. From results given in the same paper [7] it is possible to obtain a simple approximate formula corresponding to the system of reactions used by Giddings and Hirschfelder [6]. In this way by comparison we may determine the deviations between the values of the flame propagation velocity given by this formula and the results obtained by numerical integration [6], as was done for examples with nonbranching reactions [1-3].

The system of reactions in which A is the original material, P the active center and C the reaction product is written in agreement with that given in the earlier paper [7] in the form:



The right hand expressions give the rate of evolution (absorption) of heat. Here h_i is the thermal effect of the reaction (cal/mole); K_1 and W are the reaction rate constants ($\text{g}^2/\text{cm}^3 \cdot \text{mole} \cdot \text{sec}$); R is the rate of chain initiation (mole per $\text{cm}^3 \cdot \text{sec}$); n is the concentration of P (mole/g of the mixture); n_A is the concentration of A (mole/g of the mixture); T' is the temperature ($^{\circ}\text{K}$). It is assumed, in agreement with the earlier work of the author [1-5], that $R = R(T')$ and $F = F(T')$.

The flame propagation velocity u_0 (cm/sec) from an earlier investigation [7] will be determined, by the relation

$$u_0 = \frac{1}{\rho_0} \eta p_*, \quad (1)$$

where p_* is found from the equation

$$p_*^6 \eta A_1 - p_*^4 (\eta^2 A_2 + \eta A_3 + A_5) - p_*^2 (\eta A_4 - A_6 - \eta A_7 + A_8) + A_9 = 0, \quad (2)$$

the coefficients of which are calculated from the formulae

$$A_1 = 4c_m D_m^2 h_w, \quad (3)$$

$$A_2 = (c_m + lh_w)^2 r^2 W_m, \quad (4)$$

$$A_3 = 2D_m r [(c_m - lh_w) Q_{\Sigma m} + 2c_m V_m h_w - t(c_m + lh_w) X_m], \quad (5)$$

$$A_4 = r^2 [lQ_{\Sigma m}^2 - V_m (c_m - lh_w) Q_{\Sigma m} - c_m V_m^2 h_w], \quad (6)$$

$$A_5 = 4D_m^2 (t^2 X_m + \Phi_{Rm} + tQ_{\Sigma m}) h_w, \quad (7)$$

$$A_6 = 2D_m t r (Q_{\Sigma m} + V_m h_w) Q_{\Sigma m}, \quad (8)$$

$$A_7 = 2r^2 (c_m + lh_w) (R_m h_w + \Phi_{Rm}) W_m, \quad (9)$$

$$A_8 = 2D_m r [(R_m h_w - \Phi_{Rm}) Q_{\Sigma m} + 2t(R_m h_w + \Phi_{Rm}) X_m - 2V_m h_w \Phi_{Rm}] \quad (10)$$

$$A_9 = r^2 [(Q_{\Sigma m} R_m + V_m h_w R_m - V_m \Phi_{Rm}) Q_{\Sigma m} - \Phi_{Rm}^2 W_m - (V_m^2 \Phi_{Rm} + 2W_m R_m \Phi_{Rm} + X_m R_m^2) h_w] \quad (11)$$

In formulae (1) - (11) the following meanings are given to the symbols: ρ is the density (g/cm³); c is the specific heat (cal/g°C); D_p is the diffusion coefficient of the active center (cm²/sec); λ is the thermal conductivity of the mixture (cal/cm·sec°C); $D = \rho D_p$, $T = T' - T_0'$, $r = T_m (T_b - T_m)$, $T_m = 0.5 T_b$, $Q_{\Sigma} = Q + Q_V$.

$$l = \frac{n_T - n_0}{T_b}, \quad t = n_0 + lT_m \text{ \& \& } \eta = \frac{4\lambda_0}{c_0 T_m}.$$

The index "0" refers to the initial condition of the fresh mixture ($T' = T_0'$), the index \underline{b} refers to the condition at the burning temperature ($T' = T_b$) and the index \underline{m} refers to the conditions corresponding to the maximum value of the temperature gradient [1, 4] ($T' = T_m'$). In the earlier work [7] the expression $W(n^2 - n_b^2)$ was used for the rate of second order chain breaking which at $T' = T_b$ became zero. This was necessary because it was assumed from the method applied earlier [1] that $R(T_b) = 0$. Here, it is understood that $R(T_b) = W(T_b) n_b^2$ and therefore there is no need in this report to know the velocity of the second order chain breaking.

For systems with continuous branching reactions, the formulae (1) - (11) may be simplified if it is assumed that the initial and final concentrations of the active center are equal to zero ($n_0 \approx n_b \approx 0$, i.e., $l \approx t \approx 0$). This type of simplification for systems with continuous branching reactions is possible because the concentration of the active center in the reaction zone occurs in these systems more than the concentration of active centers at the temperature of combustion. But even in the simplified form, the expression A_1 remains complicated. It was shown before [1-4] that at the usual rates for chain initiation, their effect on the value of the flame propagation velocity

was small. This same conclusion may also be derived from the relations obtained before [5, 7]. But assuming that $R_m \approx 0$ (and in addition $\Phi_R \approx 0$), instead of (2) - (11), we obtain new formulae ($A_5^* = A_6^* = A_7^* = A_8^* = A_9^* = 0$):

$$\begin{aligned} p_*^4 A_1' - p_*^2 (\eta A_2' + A_3') - A_4' &= 0, \\ \text{где } A_1' &= 4D_m^2 h_w, \quad A_2' = cr^2 W_m, \quad A_3' = 2D_m r (Q_{\Sigma m} + 2V_m h_w) \text{ и} \\ A_4' &= -r^2 (Q_{\Sigma m} + V_m h_w) V_m. \end{aligned} \quad (2')$$

From (2') we obtain the equation for the determination of P_m :

$$p_*^2 = \frac{(\eta A_2' + A_3')}{2A_1'} \left[1 - \sqrt{1 + \frac{4A_1' A_4'}{(\eta A_2' + A_3')^2}} \right] \quad (12)$$

The fraction under the square root sign in (12) is always less than unity. By expanding the term under the radical sign into a series and limiting it to the two first terms, we shall find the approximate value p_* . By substituting this value in (1) we shall obtain the equation which enables us to determine the flame propagation velocity under the condition that $n_0 = n_b = R_m = 0$:

$$u_0 = \eta \frac{1}{\rho_0} \sqrt{\frac{r (Q_{\Sigma m} + V_m h_w) V_m}{\eta c_m r W_m + 2D_m (Q_{\Sigma m} + 2V_m h_w)}} \quad (13)$$

It is assumed in (13) that $F_m = 0$, i.e., it is considered that a continuous branching reaction occurs; then we obtain

$$u_0 = \frac{4\lambda_0}{\rho_0 c_0} \sqrt{\frac{c_0 (h_v + h_w) V_m^2}{2\lambda_0 c_m T_b W_m + 2c_0 D_m (h_v + 2h_w) V_m}} \quad (14)$$

This corresponds to the simplified system of reactions assumed by Giddings and Hirschfelder [6] and which consists only of the two processes: $2P \rightarrow A$ and $P + A \rightarrow C + 2P$.

From Eq. (14) the values of the flame propagation velocity were calculated for the three cases which were used by the same investigators [6] who determined the values of u_0 by integrating the corresponding system of equations numerically. In carrying out the calculations according to Eq. (14) all the original results from the same investigation were used [6]. The results of the calculations are given in the table, where it is assumed that $c_0 = c_m = \text{const}$.

The data in the table illustrate the good agreement between the values of the flame propagation velocity calculated from the approximate equation (14) and the values obtained by numerical integration [6]. This confirms the correctness of Eq. (14) and establishes the possibility of applying it for the determination of the experimental values of the rate constants of the elementary processes for a system with branched reactions, from the relations between the flame propagation velocities and the temperature. In the work carried out by Giddings and Hirschfelder it was established (see table) that with a significant variation in the diffusion coefficient of the active center, other things being equal, that the flame propagation velocity alters slightly and the latter decreases in proportion to the increase of D_p . Equation (14) permits us to explain this kind of variation in u_0 . When carrying out the numerical integration [6], Giddings and Hirschfelder assumed a very high value for the second order chain breaking rate constant, so that the first component in the denominator of Eq. (14) is approximately 10-20 times more than the second. Consequently the calculated value of u_0 is almost independent of D_p .

For a somewhat simplified system of reactions, corresponding to the oxidation of hydrogen, which in a very simplified form may be represented by a model of a unicenter reaction $2P \rightarrow A$ and $P \rightarrow 3P$, it is necessary to substitute $2V_m$ in place of V_m in Eq. (14). Thus, in this case, for the determination of the flame propagation velocity we shall obtain a new equation:

$$u_0 = \frac{4\lambda_0}{\rho_0 c_0} \sqrt{\frac{2c_0 (h_v + h_w) V_m^2}{\lambda_0 c_m T_b W_m + 2c_0 D_m (h_v + 2h_w) V_m}} \quad (15)$$

If the first term in the denominator in comparison with the second under the radical sign may be ignored (it is assumed that $W_m \approx 0$, and in addition it is necessary to assume that $h_W = 0$), then we obtain a still more simple equation for the determination of the flame propagation velocity (with $W = 0$ and $h_W = 0$).

Flame Propagation Velocities (cm/sec)

$\chi = c_0 \rho_0 D_{P_0} / \lambda_0$	1	2	0
Numerical integration [6]	55,1	54,8	58,3
From equation (14)	59,7	58,5	60,9

$$u_0 = \frac{4\lambda_0}{\rho_0 c_0} \sqrt{\frac{V_m}{D_m}} = \frac{4\lambda_0}{\rho_0 c_0} \sqrt{\frac{K_{Vm} n_{Am}}{D_m}} \quad (16)$$

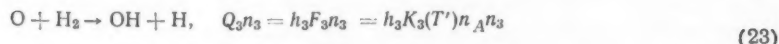
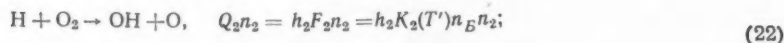
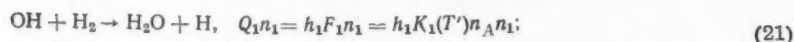
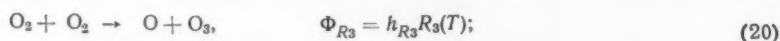
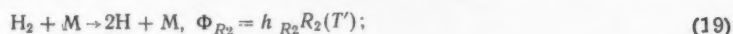
Thus if the ratio composed of the terms of the denominator under the radical sign in (15) and equal to:

$$M_W = \frac{\lambda_0}{2c_0 D_m} \frac{c_m T_b}{(h_V + 2h_W)} \frac{W_m}{V_m}, \quad (17)$$

is sufficiently small and it is possible to neglect the term $\lambda_0 c_m T_b W_m$ in comparison with the term $2c_0 D_m (h_V + 2h_W) V_m$, without exceeding the permissible error in u_0 for the given calculation, then it is possible to ignore the rate of second order chain breaking and to calculate the flame propagation velocity from Eq. (16).

Chain Branching Reaction with Three Active Centers

As an example of a chain branching reaction we shall take the example of hydrogen [8], but without considering second order chain breaking:



The right hand parts of the equations are the expressions for the rate of evolution (absorption) of heat, where h_i is the thermal effect of the reaction (cal/mole); n_1, n_2 and n_3 are the concentrations of OH, H and O (mole/g of the mixture); K_i is the reaction rate constant ($\text{g}^2/\text{cm}^3 \text{ mole} \cdot \text{sec}$); R_i is the rate of chain initiation (mole/cm³·sec); T' is the temperature (°K). It is assumed that the diffusion coefficients of H_2, O_2 and H_2O are equal to the thermal diffusion coefficients ($\lambda = c\rho D_A = c\rho D_B = c\rho D_C$) and therefore $R_i = R_i(T')$ and $F_i = F_i(T')$.

The system of equations for a laminar planar flame under these conditions, and with the system of reactions above, tends to four equations:

$$\lambda p p' - B c p + \Phi_R + Q_1 n_1 + Q_2 n_2 + Q_3 n_3 = 0, \quad (24)$$

$$D_1 p^2 n_1'' - p n_1' (B - D_1 p') + R_1 + F_2 n_2 + F_3 n_3 - F_1 n_1 = 0, \quad (25)$$

$$D_2 p^2 n_2'' - p n_2' (B - D_2 p') + R_2 + F_1 n_1 + F_3 n_3 - F_2 n_2 = 0, \quad (26)$$

$$D_3 p^2 n_3'' - p n_3' (B - D_3 p') + R_3 + F_2 n_2 - F_3 n_3 = 0, \quad (27)$$

where x is the coordinate (cm), u is the flow velocity (cm/sec), ρ is the density (g/cm³), λ is the thermal conductivity of the mixture (cal/cm·sec °C); c is the specific heat (cal/g °C), D_{p1} , D_{p2} and D_{p3} are the diffusion coefficients of OH, H and O (cm²/sec); $B = up$, $D_1 = \rho D_{p1}$, $T = T' - T_0^*$, $p = dT/dx$, $p' = dp/dT$, $n_1' = dn_1/dT$, $n_1'' = d^2 n_1/dT^2$ and $\Phi_R = \Phi_{R1} + \Phi_{R2} + \Phi_{R3}$. The boundary conditions are similar to those used earlier [1, 4] and the meaning of the indices were given above.

The equation for the determination of the flame propagation velocity u_0 (cm/sec) was obtained in an earlier investigation [5]

$$u_0 = \frac{1}{\rho_0} \eta p_*, \quad (28)$$

where p_* is found from the equation:

$$A_1 p_*^8 + A_2 p_*^6 + A_3 p_*^4 - A_4 p_*^2 - A_5 = 0, \quad (29)$$

in which $A_1 = c_m \eta$

$$A_2 = c_m \eta (F_{1m} \delta_1 + F_{2m} \delta_2 + F_{3m} \delta_3) - (Q_{1m} t_1 \omega_1 + Q_{2m} t_2 \omega_2 + Q_{3m} t_3 \omega_3) - \Phi_{Rm},$$

$$A_3 = c_m \eta F_{1m} F_{3m} \delta_1 \delta_3 - t_1 \omega_1 (Q_{1m} F_{2m} \delta_2 + Q_{1m} F_{3m} \delta_3 + Q_{2m} F_{1m} \delta_2) - \\ - t_2 \omega_2 (Q_{1m} F_{2m} \delta_1 + Q_{2m} F_{1m} \delta_1 + Q_{2m} F_{3m} \delta_3 + Q_{3m} F_{2m} \delta_3) - \\ - t_3 \omega_3 (Q_{1m} F_{3m} \delta_1 + Q_{3m} F_{1m} \delta_1 + Q_{3m} F_{2m} \delta_2 + Q_{2m} F_{3m} \delta_2) - \\ - \Phi_{Rm} (F_{1m} \delta_1^2 + F_{2m} \delta_2 + F_{3m} \delta_3) - (Q_{1m} R_{1m} \delta_1 + Q_{2m} R_{2m} \delta_2 + Q_{3m} R_{3m} \delta_3).$$

$$A_4 = F_{1m} F_{2m} F_{3m} [2c_m \eta \delta_1 \delta_2 \delta_3 + t_1 \omega_1 \delta_2 \delta_3 (h_2 + h_3) + \\ + t_2 \omega_2 \delta_1 \delta_3 (2h_1 + h_2 + h_3) + t_3 \omega_3 \delta_1 \delta_2 (h_1 + h_2)] + \\ + \Phi_{Rm} F_{1m} F_{3m} \delta_1 \delta_3 + R_{1m} \delta_1 (Q_{1m} F_{2m} \delta_2 + Q_{2m} F_{1m} \delta_2 + \\ + Q_{1m} F_{3m} \delta_3) + R_{2m} \delta_2 (Q_{1m} F_{2m} \delta_1 + Q_{2m} F_{1m} \delta_1 + Q_{3m} F_{2m} \delta_3 + Q_{2m} F_{3m} \delta_3) + \\ + R_{3m} \delta_3 (Q_{1m} F_{3m} \delta_1 + Q_{3m} F_{1m} \delta_1 + Q_{2m} F_{3m} \delta_2 + Q_{3m} F_{2m} \delta_2),$$

$$A_5 = F_{1m} F_{2m} F_{3m} \delta_1 \delta_2 \delta_3 [R_{1m} (h_2 + h_3) + R_{2m} (2h_1 + h_2 + h_3) + \\ + R_{3m} (2h_1 + h_2) - 2\Phi_{Rm}],$$

$$\text{где } \eta = \frac{4\lambda_0}{c_0 T_m}, \quad t_i = n_{i0} + l_i T_m, \quad T_m = 0.5 T_b, \quad l_i = \frac{n_{ir} - n_{i0}}{T_r}, \quad \delta_i = \frac{r}{\eta D_{im}}, \quad \omega_i =$$

$$= 1 - \frac{2q_i}{x_i}, \quad q = \frac{\mu_0}{\mu_m} \left(\frac{T_0'}{T_m} \right)^{a_i - 1} \quad \text{при } D_{pi} \sim (T')^{a_i} \quad x_i = \frac{c_0 D_{i0}}{\lambda_0} \quad r = T_m (T_b - T_m),$$

and μ is the molecular weight of the mixture.

The formula to calculate the relations between OH, H and O and the temperature $T = T' - T_0^*$ were derived earlier [5].

Due to the smallness of A_1 it is possible in practice to assume in Eq. (29) that A_1 is approximately zero. Assuming, moreover, that the rate of chain initiation is relatively small [1-4] ($R_1 \approx R_2 \approx R_3 \approx 0$), and also neglecting all the terms containing $t_1 \omega_1$ in A_2 , A_3 and A_4 (this is permissible for systems with continuous branched reactions, when the concentration of active centers in the reaction zone exceed their equilibrium values at the combustion temperature), we obtain an approximate equation [in comparison with Eq. (29)] for the determination of p_* :

$$(F_{1m}\delta_1 + F_{2m}\delta_2 + F_{3m}\delta_3) p_*^4 + (F_{1m}F_{2m}\delta_1\delta_3) p_*^2 - F_{1m}F_{2m}F_{3m}2\delta_1\delta_2\delta_3 = 0. \quad (30)$$

Obviously $F_{1m}\delta_1 > F_{2m}\delta_2$ will always apply, because $\delta_1 \approx \delta_3$, and $K_{1m} > K_{2m}$ [8]. The inequality $F_{1m}\delta_1 > F_{2m}\delta_2$, i.e., $K_{1m}n_{Am}D_{2m} > K_{2m}n_{Bm}D_{1m}$ may not be observed except in very lean mixtures, because the diffusion coefficient of the hydrogen atom is $D_{P_2} \approx 4D_{P_1}$ and $K_{1m} > K_{2m}$ [8]. Thus, it is possible to assume that

$$F_{1m}\delta_1 > (F_{2m}\delta_2 + F_{3m}\delta_3).$$

Then from (30) we obtain the more simple equation:

$$p_*^4 + F_{3m}\delta_3 p_*^2 - 2F_{2m}F_{3m}\delta_2\delta_3 = 0, \quad (31)$$

hence, omitting the negative root of the equation, we find

$$p_*^2 = \frac{1}{2} F_{3m}\delta_3 \left[\sqrt{1 + \frac{8F_{2m}\delta_2}{F_{3m}\delta_3}} - 1 \right]. \quad (32)$$

With $8F_{2m}\delta_2 < F_{3m}\delta_3$, expanding the term under the radical sign in (32) into a series, we obtain

$$p_*^2 = 2F_{2m}\delta_2, \quad (33)$$

from which it is clear that with $8F_{2m}\delta_2 / F_{3m}\delta_3 = 1$ the error in the determination of u_0 from (28) and (33) is 9% in comparison with the determination from (32).

Substituting (33) in (28) we obtain the simple equation for the determination of u_0 with $8K_{2m}n_{Bm}D_{P_3m} < K_{3m}n_{Am}D_{P_2m}$:

$$u_0 = \frac{4\lambda_0}{\rho_0 c_0} \sqrt{\frac{F_{2m}}{D_{2m}}} = \frac{4\lambda_0}{\rho_0 c_0} \sqrt{\frac{K_{2m}n_{Bm}}{D_{2m}}} \quad (34)$$

which was derived earlier [5] and which corresponds to the equation for the unicenter problem (16).

In the transitional region, when $8F_{2m}\delta_2$ is more than $F_{3m}\delta_3$, but not by much, it is necessary to use Eqs. (28) and (32) for the calculation of the flame propagation velocity or for the determination of the constants K_{2m} or K_{3m} from the experimental relations between u_0 and the combustion temperature. For the case when the numerator under the radical sign in Eq. (32) is many times more than the denominator, i.e., $8F_{2m}\delta_2 \gg F_{3m}\delta_3$, it is possible to derive the following equation from Eq. (32):

$$p_*^2 \approx \frac{1}{2} F_{3m}\delta_3 \sqrt{\frac{8F_{2m}\delta_2}{F_{3m}\delta_3}} = \sqrt{2F_{2m}\delta_2 F_{3m}\delta_3}, \quad (35)$$

and substituting this in Eq. (28) we obtain the equation for the determination of u_0 with $8K_{2m}n_{Bm}D_{P_3m} \gg K_{3m}n_{Am}D_{P_2m}$:

$$u_0 = \frac{4\lambda_0}{\rho_0 c_0} \sqrt[4]{\frac{K_{2m}n_{Bm}K_{3m}n_{Am}}{2D_{2m}D_{3m}}} \quad (36)$$

In order to convert Eq. (36) so that it corresponds with the formula for a model unicenter reaction, Eq. (16), it may be expressed in terms of the effective values of the branching rate constants $(K_{Vm})_{ef}$ and of the diffusion constant, multiplied by the density $(D_m)_{ef}$. Under this form Eq. (36) will be analogous to Eq. (16)

$$u_0 = \frac{4\lambda_0}{\rho_0 c_0} \sqrt{\frac{(K_{Vm})_{ef} (n_{Am})_{ef}}{(D_m)_{ef}}}, \quad (37)$$

where

$$(K_{vm}) = \sqrt{\frac{1}{2} K_{2m} \frac{n_{Bm}}{(n_{Am})_{ef}} K_{3m} \frac{n_{Am}}{(n_{Am})_{ef}}}, \quad (38)$$

$$(D_m)_{ef} = \sqrt{D_{2m} D_{3m}} \quad (39)$$

Let us examine Eqs. (34) and (36) or (37). The still small value of $F_{2m} = K_{2m} n_{Bm}$ entering into the expression for the rate of the branching process, Eq. (22), indicates that the flame propagation velocity when hydrogen is burnt is determined mainly by the value F_{2m} , proportional to the rate constant of the branching process in Eq. (22), which follows from Eq. (34). In the other case, when the small value $F_{3m} = K_{3m} n_{Am}$ enters into the expression for the rate of the reaction given in Eq. (23), the flame propagation velocity [Eq. (36)] depends on both values, F_{2m} and F_{3m} , proportional to the constants K_{2m} and K_{3m} , which to an equal degree determine the effective constant of the branching process, in Eq. (38). The solution of the problem of flame propagation of hydrogen, burning in oxygen, proposed in the present section was obtained without considering second order chain breaking. But Eqs. (34) and (36) or (37) make it possible to determine the parameters and constants for a model uncenter reaction which corresponds to Eq. (15) or (16). Thus using Eqs. (15), (16) and (17), it is possible with the aid of Eq. (34) or (37) to estimate the effect of the process of second order chain breaking on the value of the flame propagation velocity in a real system with three active centers. Moreover, the confirmation of formula (14) from the results of the numerical integration (see the table) by the comparison of Eq. (16) with Eqs. (34) and (37) verifies that the solution obtained for a real system with three active systems is correct. In this way it is shown that Eqs. (28) with (30) or (32) and (34) and (36) may be used for determining the experimental values of the rate constants of the elementary processes from the relations between the flame propagation velocity and the combustion temperature.

Examples of Numerical Calculations

Equation (34) was used for determining the experimental value of the constant in Eq. (22) from the relation between u_0 and the combustion temperature for two mixtures: 1) a mixture of composition: $0.72H_2 + 0.2795O_2 + 0.0015N_2$; $\lambda_0 = 2.6 \cdot 10^{-4}$, $D_{P20} = 1.35$ (atom H), $a_2 = 1.9$; $T_0^* = 293^\circ K$ and $T_b^* = 3045^\circ K$; 2) a mixture of composition $0.43 H_2 + 0.57$ air; $\lambda_0 = 1.6 \cdot 10^{-4}$, $D_{P20} = 1.15$ (atom H), $a_2 = 1.9$; $T_0^* = 293^\circ K$ and $T_b^* = 2126^\circ K$. The combustion temperature was calculated taking dissociation into account. The diffusion coefficients were calculated from the effective radius of hydrogen, using the method of Clingman, Brokaw and Pease [9]. The thermal conductivity of the mixture was determined from experimental results given in the book of Hirschfelder, Curtiss and Bird [10] for mixtures of H_2 and O_2 .

The experimental values of the constant K_2^0 were determined for the given two mixtures from two sources: 1) from the data of Jahn [11] the ratio of the flame propagation velocities is 3.39 and the rate constant found from (34) is $K_2^0 = 1.32 \cdot 10^{14} \cdot \exp(-14000/RT^*)$ (cm³/mole·sec), 2) from the more recent data of Bartolome [12] the ratio of the flame propagation velocities is 3.80 and the constant found from (34) is $K_2^0 = 4.72 \cdot 10^{14} \exp(-16300/RT^*)$ (cm³ per mole sec).

The values of K_2^0 obtained are found to be in satisfactory agreement with the value $K_2^0 = 5.66 \cdot 10^{13} \exp(-15100/RT^*)$ and we found to be independent of the flame by the kinetic methods of Karmilov, Nalbandyan and Semenov [13, 14]. In order to obtain a more precise value of K_2^0 the given calculation should be carried out with a greater concentration of hydrogen (rich mixtures). Subsequently, from the relation between the velocity of flame propagation and the temperature in mixtures with low concentrations of hydrogen (lean mixtures), it should be possible, by means of Eqs. (28) and (32), to determine the experimental value of the reaction rate constant K_3^0 , given in Eq. (23). From Eq. (34) it follows that the velocity of flame propagation is proportional to the thermal conductivity of the mixture and inversely proportional to the square root of the diffusion coefficient of the hydrogen atom. Mellish and Linnert [15] derived the ratio of the velocities of flame propagation for two mixtures ($0.21H_2 + 0.11O_2$), the first of which contained 0.68 helium and the second, 0.68 argon. The value of this ratio, obtained experimentally, was 2.40. In the same investigation the authors found the ratio of the thermal conductivities to be 3.76 and the square root of the ratio of diffusion coefficients of the hydrogen atom 1.32. The theoretical ratio of the velocities of flame propagation calculated with the help of Eq. (34) is $3.76/1.32 = 2.85$, which proves to be slightly greater than the experimental result. However, this agreement should be recognized as satisfactory, bearing in mind the difficulties connected with the determination of the transfer coefficients, the possible errors in the approximate theoretical equations and the inaccuracies of the experimental results.

From Eqs. (14) or (15) it follows that if the first term in the denominator under the square root sign is more than the second, then u_0 is proportional to the square root of the thermal conductivity (i.e., $u_0 \sim \sqrt{\lambda_0}$) and is practically independent of the value D_{pm} . In the case when helium replaces argon the result should be $(u_0)_{He}/(u_0)_A \sqrt{\lambda_{He}/\lambda_A} = 1.94$. The experimental ratio of 2.40 was found to lie within the limits of 1.94-2.85. From this it obviously follows that second order chain breaking plays a certain role in the case in question, and it is possible to solve the opposite problem — the determination of the experimental value of the second order chain breaking rate constant from the ratio 2.40. Hence, it is found that $M_W = 0.52$ [Eq. (17)] and therefore the calculation $K_{Wm} = W_m \mu_m / \rho_m^3$ can only be a roughly estimated calculation. K_{Wm} calculated from Eq. (15) using the ratio 2.40 was found to be approximately equal to $K_{Wm} \approx 10^{17} \text{ cm}^6/\text{mole}^2 \cdot \text{sec}$.

The author wishes to express his sincere thanks to V. N. Kondrat'ev and N. N. Semenov for the discussion of the work and for their valuable advice.

SUMMARY

1. A solution to the problem of flame propagation in systems with chain branching reactions including three active centers has been obtained. The approximate solution was shown to be correct by comparing a similar solution obtained for a model unicenter reaction with the results obtained by numerical integration of the corresponding system of differential equations.

2. It has been shown possible with the help of the solutions obtained to determine the experimental values of the constants of the elementary reactions from the relations between the velocity of flame propagation and the combustion temperature and transfer coefficients. The numerical determination of the values of the constants was made for two examples for the flame of burning hydrogen.

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ORGANIC AND BIOLOGICAL CHEMISTRY

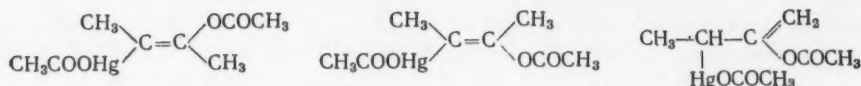
PRODUCTS OF MERCURIC SALT ADDITION TO DISUBSTITUTED ACETYLENES

A. N. Nesmeyanov, A. E. Borisov, I. S. Savel'eva, and
M. A. Osipova

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR
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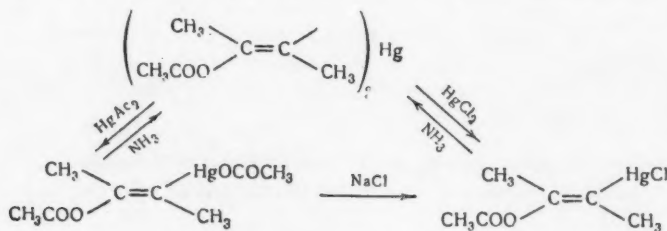
The addition reaction of mercuric acetate to dimethylacetylene was described in one of our previous papers [1]. Three products are thus formed, isolated, and characterized as chloromercury compounds (by precipitation with NaCl): *trans*-1-methyl-2-acetoxy-1-propen-1-ylmercury chloride melting at 140°, its *cis*-isomer melting at 95-96°, and its structural isomer - 1-methyl-2-acetoxy-2-propen-1-ylmercury chloride melting at 130°; the symmetry of these compounds was also described. The geometric configuration of isomeric 1-methyl-2-acetoxy-1-propen-1-ylmercury chloride and the corresponding R_2Hg compounds were established on the basis of IR-absorption spectra [2]. In the present communication we will describe an acetate not previously isolated which corresponds to the above-mentioned organomercury chloride.

By reaction of di-(*trans*-1-methyl-2-acetoxy-2-propen-1-yl)-mercury, its *cis-cis*-isomer, and di-(1-methyl-2-acetoxy-2-propenyl)-mercury with mercuric acetate in benzene with a trace of glacial acetic acid three corresponding organometallic mercury compounds of formula $C_8H_{12}O_4Hg$, which we designated as α -isomer (m. p. 120-121°), β -isomer (m. p. 81.5-83°), and γ -isomer (m. p. 106-107.5°), were formed and the following structures are attributed to them:

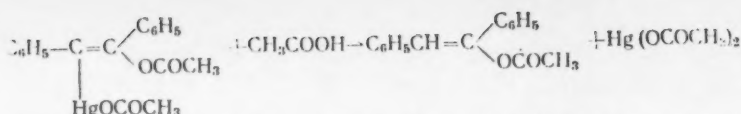


These three compounds are very easily soluble in water and in the usual organic solvents. All three α -, β -, and γ -isomers were converted to the corresponding chlorides by precipitation from a saturated aqueous NaCl solution. Thus the α -isomer gave *trans*-1-methyl-2-acetoxy-1-propen-1-ylmercury chloride melting at 140°, the β -isomer gave the *cis*-chloromercury compound melting at 95°, and from the γ -isomer was obtained 1-methyl-2-acetoxy-2-propen-1-ylmercury chloride melting at 130°.

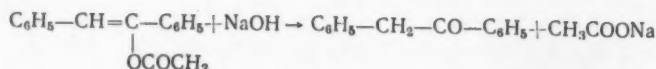
The α -, β -, and γ -isomers are easily made symmetrical (analogous to chloromercury compounds [1] in ammoniacal carbon tetrachloride solution with formation in each case of all the original symmetrical compound. The scheme illustrates the conversion of geometrical isomers of chloromercury compounds:



By reaction of tolane with mercuric acetate in glacial acetic acid α -acetoxy- β -acetoxymercurystilbene, together with α -acetoxy- β -chloromercurystilbene, which is formed at very high temperature, is formed; Drefana and Shaaf [3] characterized the latter as the *cis*-isomer of α -acetoxy- β -chloromercurystilbene; its formation is connected to a secondary process and the yield depends on temperature.



Later the *cis* configuration of α -acetoxy- β -chloromercurystilbene, obtained from the acetomercury compound [4], was described. α -Acetoxystilbene is formed easily by reaction of hydrochloric acid with the correspond chloromercury compound; its ester group is easily saponified by aqueous sodium stannite solution, from which benzylphenylketone is obtained in good yield.



The reaction of di-(1,2-diphenyl-2-acetoxyethen-1-yl)mercury with thallium trichloride led to 1,2-diphenyl-2-acetoxyethen-1-ylthallium dichloride, but its reaction with metallic mercury gave 1,2-di-phenyl-2-acetoxyethen-1-ylmercury chloride.

EXPERIMENTAL

Trans-1-methyl-2-acetoxy-1-propen-1-ylmercury acetate. To a solution of 0.5 g (0.00117 M) of di-(trans-1-methyl-2-acetoxy-1-propen-1-yl)mercury in 5 ml of benzene was added 0.37 g (0.00117 M) of mercuric acetate and 5 drops of glacial acetic acid. The mixture was stirred until the solids dissolved. The end of the reaction was defined as a negative reaction for mercuric ion (test with NaOH solution did not give a yellow precipitate of mercuric oxide). An hour after the beginning of the reaction the solvent was distilled; the residue (0.89 g) was recrystallized from 6 ml of carbon tetrachloride, from which was obtained 0.75 g of trans-1-methyl-2-acetoxy-1-propen-1-ylmercury acetate; m. p. 120-121°. From the mother liquor an additional 0.06 g of substance m. p. 119-120° separated. The total yield was 0.81 g, which is 91% of theoretical. Found: C 25.63, 25.73; H 3.45, 3.22%. $\text{C}_8\text{H}_{12}\text{O}_4\text{Hg}$. Calculated: C 25.77; H 3.24%.

Cis-1-methyl-2-acetoxy-1-propen-1-ylmercury acetate. From 0.19 g (0.00044 M) of di(cis-1-methyl-2-acetoxy-1-propen-1-yl)mercury and 0.14 g (0.00044 M) of mercuric acetate in 2 ml of benzene with 4 drops of glacial acetic acid was obtained by an analogous route 0.26 g (80%) of cis-1-methyl-2-acetoxy-1-propen-1-ylmercury acetate melting at 81.5-83°. Found: C 25.62, 25.70; H 3.36, 3.28%. $\text{C}_8\text{H}_{12}\text{O}_4\text{Hg}$. Calculated: C 25.77; H 3.24%.

1-Methyl-2-acetoxy-2-propen-1-ylmercury acetate. By the route described for cis- and trans-acetomercury compounds, 1-methyl-2-acetoxy-2-propen-1-ylmercury acetate melting at 106-107.5° (from carbon tetrachloride) was obtained from di-(1-methyl-2-acetoxy-2-propen-1-yl)mercury and mercuric acetate in benzene solution in 94% of theoretical yield. Found: C 25.89, 25.88; H 2.98, 3.07%. $\text{C}_8\text{H}_{12}\text{O}_4\text{Hg}$. Calculated: C 25.77; H 3.24%.

Conversion of acetomercury compounds to chloromercury compounds. To a solution of 0.2 g (0.000536 M) of trans-1-methyl-2-acetoxy-1-propen-1-ylmercury acetate in 2 ml of glacial acetic acid was added a two-fold excess of saturated sodium chloride solution. The precipitate which separated was filtered off, washed with water, and dried. After recrystallization from carbon tetrachloride 0.14 g (74%) of trans-1-methyl-2-acetoxy-1-propen-1-ylmercury chloride melting at 140° was obtained. A mixed sample with a known sample of (I) did not give melting point depression.

Under analogous conditions 0.13 g (72%) of cis-1-methyl-2-acetoxy-1-propen-1-ylmercury chloride melting at 93-94° was obtained from 0.2 g of cis-1-methyl-2-acetoxy-1-propen-1-ylmercury acetate; this melted at 94-95° after repeated crystallization from carbon tetrachloride. A melting point determination with a known sample of (I) did not give melting-point depression.

The chloromercury compound melting at 129° was obtained by the same route from 0.5 g (0.00134 M) of 1-methyl-2-acetoxy-2-propen-1-ylmercury acetate and saturated NaCl solution. Literature data; m. p. 130° [2]; yield 90%.

Preparation of symmetrical trans-acetomercury compounds. Dry ammonia was passed through a solution of 0.5 g (0.00134 M) of trans-1-methyl-2-acetoxy-1-propen-1-ylmercury acetate in 30 ml of dry carbon tetrachloride for 30 min. The precipitate which formed was filtered off, and the filtrate was distilled. The dry residue of

di-(trans-1-methyl-2-acetoxy-1-propen-1-yl)mercury melted at 110-113°. Yield 0.15 g (54%). After recrystallization from ligroin, m. p. 113-114°. A mixed determination with a known sample did not give melting-point depression.

By an analogous route 0.33 g (67%) of di-(cis-1-methyl-2-acetoxy-1-propen-1-yl)mercury, which after recrystallization from ligroin melted at 100-100.5°, was prepared from 1 g of cis-1-methyl-2-acetoxy-1-propen-1-ylmercury acetate in 50 ml of carbon tetrachloride. Literature data [1]; m. p. 101-102°.

By the same route 0.2 g (71%) of di-(1-methyl-2-acetoxy-2-propen-1-yl)mercury melting at 130° (from ligroin) was obtained from 0.5 g (0.00134 M) of 1-methyl-2-acetoxy-2-propen-1-ylmercury acetate. Literature data [1]; m. p. 130°.

1,2-Diphenyl-2-acetoxyethen-1-ylmercury acetate. To 10 g (0.056 M) of toluene in 10 ml of glacial acetic acid was added gradually 18 g (0.056 M) of mercuric acetate in 100 ml of glacial acetic acid at 70-80°, and the reaction products were mixed at 95-96° for 2.5 hr. The cooled solution was filtered, and the reaction product was precipitated with a saturated solution of sodium acetate. The 1,2-diphenyl-2-acetoxyethen-1-ylmercury acetate which separated melted at 140-141° (recrystallization from methanol). A second recrystallization did not change the melting point. Found: C 43.35, 43.12; H 3.09, 3.17; Hg 40.08, 40.25%. $C_{18}H_{16}O_4Hg$. Calculated: C 43.50; H 3.22; Hg 40.39%.

Decomposition of 1,2-diphenyl-2-acetoxyethen-1-ylmercury chloride with hydrochloric acid. 1,2-Diphenyl-2-acetoxyethen-1-ylmercury chloride (m. p. 138°; 5 g, 0.01 M) was heated on a water bath for 40 min with 15 ml of concentrated hydrochloric acid. After cooling and addition of 15 ml of water the oil which formed on the surface crystallized. The crystals which were filtered off melted at a constant 100.5-101° after three recrystallizations from methanol. The yield of 1,2-diphenyl-2-acetoxyethene was 63%. Found: C 80.01, 80.33; H 6.12, 5.87%. $C_{16}H_{14}O_2$. Calculated: C 80.67; H 5.83%.

Benzylphenyl ketone. To 0.5 g (0.00112 M) of 1,2-diphenyl-2-acetoxyethene in 25 ml of ethanol was added 0.2 g (0.01 M) of sodium stannite (prepared from 0.12 g of $SnCl_2 \cdot 2H_2O$ and 0.08 g of NaOH). The filtrate was diluted with 100 ml of water; the precipitate formed was separated and melted at 48-50° after recrystallization from ethanol; weight 0.26 g (90%). Found: C 85.61, 85.70; H 6.35, 6.33%. $C_{14}H_{12}O_2$. Calculated: C 85.71; H 6.12%.

Reaction of di-(1,2-diphenyl-2-acetoxyethen-1-yl)mercury with thallium trichloride. Di-(1,2-diphenyl-2-acetoxyethen-1-yl)mercury (2.6 g, 0.0038 M; m. p. 171°) in 50 ml of benzene was mixed with shaking with 1.2 g (0.0038 M) of thallium trichloride. The precipitate which formed three hours later was removed, washed with hot benzene, and recrystallized from a mixture of ethanol and water (1:1). On heating the substance decomposed at 133-134°; weight 1.81 g (91.5%). Found: C 37.62; H 2.63; Cl 13.19%. $C_{16}H_{13}HCl_2$. Calculated: C 37.46; H 2.59; Cl 13.83%.

Reaction of 1,2-diphenyl-2-acetoxyethen-1-ylthallium dichloride with metallic mercury. A solution of 1 g (0.0019 M) of 1,2-diphenyl-2-acetoxyethen-1-ylthallium dichloride in 20 ml of acetone and 2.04 g (0.0099 M) of metallic mercury was shaken in a sealed tube at 35-40° for 30 hr. The solution was filtered from metallic mercury and thallium chloride. The solvent was removed from the filtrate; after recrystallization from methanol the dry residue melted at 138°. A mixed melting point with a known sample of 1,2-diphenyl-2-acetoxyethen-1-ylmercury chloride melted without depression; yield 71%.

SUMMARY

The syntheses and properties of cis- and trans-1-methyl-2-acetoxy-1-propen-1-ylmercury acetate, 1-methyl-2-acetoxy-2-propen-1-ylmercury acetate and 1,2-diphenyl-2-acetoxy-1-ylmercury* acetate are described.

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* Publisher's note: should probably read 1,2-diphenyl-2-acetoxy-ethen-1-ylmercury acetate.

TELOMERIZATION OF ETHYLENE WITH POLYCHLOROALKANES CONTAINING THE CCl₂Br GROUP

V. N. Kost and R. Kh. Freidlina

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR

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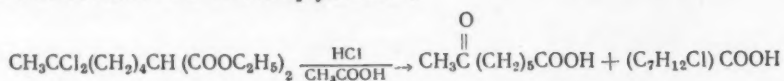
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The reaction of polyhaloalkanes with olefins, particularly with ethylene, had been used recently for building carbon chains by two atoms (addition reaction) or by several atoms, in multiples of two (telomerization reaction). In this work we used the telomerization reaction to synthesize compounds containing the dichloromethyl group. Similar compounds were of interest to us, in particular, in a scheme for studying comparative reactivity of different polyhalo groups, and also as intermediates for the syntheses of polyfunctional compounds. Substances which contain the trichloromethyl group enter into free-radical addition or telomerization reactions with difficulty; only in the presence of activating substituents, for example, trichloroacetate esters and so forth, does such a reaction occur. A compound, containing the CCl₂Br group, obviously must enter an addition reaction very easily.

In our publication we described the reaction of ethylene in heptane solution with the following compounds containing the dichlorobromomethyl group: CH₃CCl₂Br, BrCH₂CH₂CCl₂Br, Cl(CH₂)₄CCl₂Br; benzoyl peroxide was used as initiator. Condensation products and telomers (table) were obtained in good conversions.

Telogen	Reaction product formed	
CH ₃ CCl ₂ Br	CH ₃ CCl ₂ (CH ₂ CH ₂) _n Br	n = 1, 2, 3
BrCH ₂ CH ₂ CCl ₂ Br	BrCH ₂ CH ₂ CCl ₂ (CH ₂ CH ₂) _n Br	n = 1, 2
Cl(CH ₂) ₄ CCl ₂ Br	Cl(CH ₂) ₄ CCl ₂ (CH ₂ CH ₂) _n Br	n = 1, 2

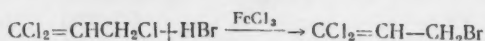
The dichloromethyl group in these compounds is easily hydrolyzed with concentrated sulfuric acid even at a temperature of 35-50°. By hydrolysis of 2,2-dichloro-6-bromohexane and 1,5,5-trichloro-9-bromononane the corresponding ketones were obtained in good yields. The action of ferric chloride on 2,2-dichloro-6-bromohexane led to dehydrochlorination with formation of chlorobromohexene. With nucleophilic reagents, for example with sodium malonic ester, bromine is displaced. Thus, 2,2-dichloro-7-dicarboxyheptane was obtained from 2,2-dichloro-6-bromohexane and sodium malonic ester; this upon hydrolysis with hydrochloric acid and subsequent decarboxylation formed a mixture of chlorooctenoic and 7-ketocaprylic acids.



Thus, the dichloromethyl group undergoes hydrolysis or dehydrochlorination during ester hydrolysis.

The initial compounds containing the dichlorobromomethyl group were obtained by addition of hydrogen bromide to 1,1-dichloroethylene, 1,1-dichloro-3-bromopropene-1, and 1,1,5-trichloropentene-1 in the presence of ferric chloride. Often a mixture of products, depending (obviously) on a slow addition reaction and loss of hydrogen halide, was formed during these reactions. We were able to obtain good yields of addition products using the lowest possible reaction temperature (at which the reaction still would go) and a minimum amount of ferric chloride. In the case of the reaction with 1,1,5-trichloropentene-1 we were restricted to a 50% conversion to pure product. It is interesting

to point out that in the reaction of hydrogen bromide with 1,1,3-trichloropropene-1 in the presence of ferric chloride the interchange of allylic chloride atom with bromine occurs.



The dichlorobromopropene obtained has low constants owing to the presence of low-boiling contaminants, e.g., tetrachloropropene. Similarly, 1,1,2,3-tetrachloropropene-1 reacts with hydrogen bromide forming 1,1,2-trichloro-3-bromopropene-1 in nearly quantitative yield.

EXPERIMENTAL

Addition of hydrogen bromide to 1,1-dichloroethylene. While cooling with a mixture of ice and salt dry hydrogen bromide was added to ferric chloride in 97 g of 1,1-dichloroethylene until the increase in weight was 82 g. After washing with water, soda solution, and drying over calcium chloride the product was distilled through a column. Thus 140 g (78% of theory) of 1,1-dichloro-1-bromoethane boiling at 98-99° was isolated, n_D^{20} 1.4818, d_4^{20} 1.7465; found MR 29.02; calculated MR 28.93. Found: C 13.54, 13.70; H 1.69, 1.74%. $\text{C}_2\text{H}_3\text{Cl}_2\text{Br}$. Calculated: C 13.51; H 1.70%. Literature data [1]: b. p. 98°. 1,1,1-Trichloroethane, b. p. 76-77° and chlorodibromoethane, b. p. 123-125° were also separated from the reaction products.

Addition of hydrogen bromide to 1,1,5-trichloropentene-1. Hydrogen bromide was passed through a solution of 0.4 g of ferric chloride in 86 g of trichloropentene with ice cooling of the flask until the weight increase was 25 g. After work up and careful distillation through a column under vacuum 39 g of starting trichloropentene and 57 g (82% of theory, based on trichloropentene reactions) of 1,1,5-trichloro-1-bromopentane boiling at 85-86° (3 mm) were isolated; n_D^{20} 1.5142, d_4^{20} 1.6090; found MR 47.62; calculated MR 47.66. Found: C 23.76, 23.64; H 3.19, 3.21%. $\text{C}_5\text{H}_5\text{Cl}_3\text{Br}$. Calculated: C 23.60; H 3.17%.

Reaction of hydrogen bromide with 1,1,3-trichloropropene-1 and 1,1-dichloro-3-bromopropene-1. Hydrogen bromide was passed through a solution of 0.4 g of ferric chloride in 150 g of trichloropropene with mixing until the weight increase was 61 g. After the work-up the mixture was distilled through a column under vacuum. As a result of the distillation 20 g of starting trichloropropene, 106 g of a fraction boiling at 36-37° (2 mm); n_D^{20} 1.5321, d_4^{20} 1.7346, which consists mainly of 1,1-dichloro-3-bromopropene (literature data [2]: b. p. 45.1° (10 mm); n_D^{20} 1.5363, d_4^{20} 1.7593) and also 15 g of 1,1-dichloro-1,3-dibromopropane boiling at 71° (8 mm); n_D^{20} 1.5450, d_4^{20} 2.0714 were separated. Also other substances not studied more closely were present in intermediate fractions. By addition of hydrogen bromide to 100 g of the dichlorobromopropene obtained, 1,1-dichloro-1,3-dibromopropane boiling at 71° (8 mm); was isolated in 60% yield; n_D^{20} 1.5450, d_4^{20} 2.0772; found MR 41.22; calculated MR 41.32. Found: C 13.39, 13.51; H 1.50, 1.52%. $\text{C}_3\text{H}_4\text{Cl}_2\text{Br}_2$. Calculated: C 13.31; H 1.49%.

Reaction of hydrogen bromide with 1,1,2,3-trichloropropene-1. Hydrogen bromide was passed through 36 g of tetrachloropropene and 0.1 g of ferric chloride at room temperature. 1,1,2-Trichloro-3-bromopropene boiling at 76-77° (17 mm); n_D^{20} 1.5550, d_4^{20} 1.8820 was separated (35.5 g, 80% of theory) from some starting tetrachloropropene by distillation. Literature data [3]: b. p. 78-79° (19 mm); n_D^{20} 1.5550, d_4^{20} 1.8835.

Telomerization of ethylene with 1,1-dichloro-1-bromoethane. In a 0.5-liter autoclave were placed 113 g of bromodichloroethane, 100 ml of n-heptane, 1 g of benzoyl peroxide, and 50 ml of water. The air in the autoclave was displaced by ethylene, after which ethylene was charged to a pressure of 75 atm. The autoclave was heated to 80-90° for 4 hr. The maximum pressure during heating was 90 atm, but was 70 atm at 90° at the end of the reaction. The reaction mixture, after washing, drying, and removal of solvent, was distilled through a column under vacuum. 2,2-Dichloro-4-bromobutane (108 g) boiling at 72-73° (22 mm); n_D^{20} 1.4938, d_4^{20} 1.5768; found MR 38.01; calculated MR 38.17. Found: C 23.34, 23.44; H 3.41, 3.45%. $\text{C}_4\text{H}_7\text{Cl}_2\text{Br}$. Calculated: C 23.33; H 3.43%, and 50 g of 2,2-dichloro-6-bromohexane boiling at 118° (22 mm); n_D^{20} 1.4950, d_4^{20} 1.4284; found MR 47.44; calculated MR 47.41. Found: C 31.13, 31.06; H 4.74, 4.73%. $\text{C}_6\text{H}_{11}\text{Cl}_2\text{Br}$. Calculated: C 30.80; H 4.74% were obtained.

From the distillation residues of several experiments 2,2-dichloro-8-bromooctane boiling at 82-83° (1 mm); n_D^{20} 1.4930, d_4^{20} 1.3452; found MR 56.61; calculated MR 56.64. Found: C 36.64, 36.67; H 5.63, 5.64%. $\text{C}_8\text{H}_{15}\text{Cl}_2\text{Br}$. Calculated: C 36.67; H 5.77% was separated.

Telomerization of ethylene with 1,1,5-trichloro-1-bromopentane. The experiment was conducted like the previous one. From a charge of 150 g of trichlorobromopentane, 1 g of benzoyl peroxide, 100 ml of heptane, 50 ml

of water and 70 atm of ethylene pressure (the maximum pressure during heating was 95 atm) were obtained 100 g of 1,5,5-trichloro-7-bromoheptane boiling at 92-93° (2 mm); n_D^{20} 1.5150, d_4^{20} 1.5061; found MR 56.56; calculated MR 56.89. Found: C 29.88, 30.04; H 4.35, 4.36%. $C_7H_{12}Cl_3Br$. Calculated: C 29.76; H 4.28%, and 35 g of 1,5,5-trichloro-9-bromononane boiling at 132-133° (2 mm); n_D^{20} 1.5130, d_4^{20} 1.4119; found MR 66.10; calculated MR 66.13. Found: C 35.39, 35.33; H 5.33, 5.33%. $C_9H_{16}Cl_3Br$. Calculated: C 34.81; H 5.20%.

Telomerization of ethylene with 1,1-dichloro-1,3-dibromopropane. The experiment was conducted as above. Dichlorodibromopropane (100 g), 100 ml of heptane, 1 g of benzoyl peroxide, and 50 ml of water were charged. Ethylene was used in the same quantity as in the previous experiment. As a result of reaction a mixture of liquid and crystalline products was obtained. After filtration, the filtrate was washed, dried, and distilled under vacuum. The substance boiling at 85-90° (2 mm) rapidly crystallized. A total of 65 g of crystalline 3,3-dichloro-1,5-dibromopentane melting at 70-71° (from heptane) was obtained. Found: C 20.44, 20.49; H 2.64, 2.64%. $C_5H_8Cl_2Br_2$. Calculated: C 20.09; H 2.70%.

3,3-Dichloro-1,7-dibromoheptane (26 g) boiling at 117-118° (2 mm) was also obtained; n_D^{20} 1.5345, d_4^{20} 1.7075; found MR 59.56; calculated MR 59.78. Found: C 25.96, 25.88; H 3.72, 3.55%. $C_7H_{12}Cl_2Br_2$. Calculated: C 25.72; H 3.70%.

Hydrolysis of 2,2-dichloro-6-bromohexane. A mixture of 24 g of dichlorobromohexane and 50 ml of concentrated sulfuric acid was stirred at 35-40° until almost the theoretical amount of hydrogen chloride was evolved. The reaction mixture was poured onto ice, the oil layer was washed with water, with soda solution, with soda again, and dried over calcium chloride. 6-Bromohexanone-2 (15 g; 83% of theory) was separated by distillation at 89° (8 mm); n_D^{20} 1.4708, d_4^{20} 1.3300; found MR 37.62; calculated MR 37.68. Literature data [4]: b. p. 104-105° (15 mm); n_D^{20} 1.4713. Found: C 40.04, 40.05; H 6.14, 6.19%. $C_6H_{11}OBr$. Calculated: C 40.24; H 6.19%.

2,4-Dinitrophenylhydrazone; m. p. 80-81° (from alcohol). Literature data [4]: m. p. 80.5-81.5°.

Hydrolysis of 1,5,5-trichloro-9-bromononane. A mixture of 15 g of trichlorobromononane and 25 ml of sulfuric acid was stirred for 30 min at 50-60°. After work-up and distillation 9.1 g (74% of theory) of 1-chloro-9-bromononane-5 boiling at 121-122° (1 mm) was isolated; n_D^{20} 1.4937, d_4^{20} 1.3235; found MR 56.20; calculated MR 56.40. Found: C 42.06, 42.31; H 6.33, 6.35%. $C_7H_{13}OBr$. Calculated: C 42.29; H 6.31%.

2,4-Dinitrophenylhydrazone; m. p. 60-61° (from alcohol). Found: C 41.14, 41.24; H 4.56, 4.54%. $C_{15}H_{19}O_4N_4Br$. Calculated: C 41.35; H 4.62%.

Reaction of 2,2-dichloro-6-bromohexane with sodiummalonic ester. To a solution of alcoholate prepared by dissolving 2.3 g of sodium in 60 ml of absolute alcohol was added 46 g of malonic ester, and then 23 g of dichlorobromohexane. The mixture was heated on a water bath for 4 hr. After dilution with water the oil which separated was washed with water and dried over calcium chloride. By distillation 24 g (77% of theory) of 2,2-dichloro-7,7-dicarboxyheptane boiling at 126-128° (2 mm) was obtained; n_D^{20} 1.4572, d_4^{20} 1.1300; found MR 75.52; calculated: MR 75.28. Found: C 49.84, 49.83; H 7.04, 7.04%. $C_{13}H_{22}O_4Cl_2$. Calculated: C 49.84; H 7.08%.

Hydrolysis (20 g) of the ester obtained was accomplished by heating in a mixture of hydrochloric and acetic acids for 12 hr. Decarboxylation of the acids formed was performed by heating under vacuum at 190°; by distillation under vacuum were obtained 5.1 g of the chlorooctenoic acid boiling at 101-102° (1 mm); n_D^{20} 1.4712, d_4^{20} 1.1188; found MR 45.18; calculated MR 45.08. Found: C 54.48, 54.32; H 7.35, 7.14%. $C_8H_{13}O_2Cl$. Calculated:



C 54.39; H 7.42%, and 2 g of an acid of the formula $C_8H_{14}O_3$, apparently of the structure $CH_3C-(CH_2)_5COOH$ boiling at 114-115° (1 mm); m. p. 30-32° (from heptane). Found: C 60.08, 60.20; H 8.88, 8.91%. Calculated: C 60.74; H 8.92%. Literature data [5]: b. p. 184-185 (15 mm); [6]: b. p. 29-30°.

Reaction of 2,2-dichloro-6-bromohexane with anhydrous ferric chloride. Dichlorobromohexane (20 g) and 0.5 g of ferric chloride were heated at 40-60° until the evolution of hydrogen chloride ceased. The reaction mixture was washed with water, with soda solution, again with soda, and dried over calcium chloride. By distillation 11.8 g (70% of theory) of chlorobromohexene boiling at 73-74° (10 mm) was obtained; n_D^{20} 1.4960, d_4^{20} 1.3689; found MR 42.15; calculated MR 42.07. Found: C 36.29, 36.43; H 4.75, 4.79%. $C_6H_{10}ClBr$. Calculated: C 36.49; H 5.10%.

SUMMARY

1. The telomerization of ethylene with 1,1-dichloro-1-bromoethane, 1,1,5-trichloro-1-bromopentane and 1,1-dichloro-1,3-dibromopropane afforded telomers of the structures: $\text{CH}_3\text{CCl}_2(\text{CH}_2\text{CH}_2)_n\text{Br}$, where $n = 1, 2, 3$; $\text{Cl}(\text{CH}_2)_4\text{CCl}_2(\text{CH}_2\text{CH}_2)_n\text{Br}$ and $\text{Br}(\text{CH}_2)_2\text{CCl}_2(\text{CH}_2\text{CH}_2)_n\text{Br}$, where $n = 1, 2$.

2. Compounds containing the $-\text{CCl}_2$ group are easily hydrolyzed by the action of concentrated H_2SO_4 with formation of ketones and are dehydrochlorinated by FeCl_3 with formation of unsaturated chlorohydrocarbons.

3. The addition reaction of HBr to compounds of the type $\text{X}(\text{CH}_2\text{CH}_2)_n\text{CH} = \text{CCl}_2$ occurs smoothly in the presence of FeCl_3 .

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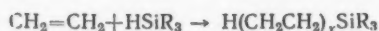
All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

REARRANGEMENT DURING THE PROCESS OF THERMAL TELOMERIZATION OF ETHYLENE WITH SILICON HYDRIDES

R. Kh. Freidlina, Yu. P. Egorov, E. Ts. Chukovskaya,
Tsao, I. and E. D. Lubuzh

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR
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Thermal telomerization of ethylene with silicon hydrides, occurring according to the scheme:



opens new methods for synthesis and study of silanes containing long-chain radicals. The reaction is conducted by heating to 250-300° under a pressure of 100-500 atm in the absence of any catalyst or initiator [1-4]. But in cases studied up to now (Table 1) only silanes, for which $x \leq 6$ were isolated.

TABLE 1. Telomerization of Ethylene with Silicon Hydrides

Silane used	Telomer-homologs	x	Lit. reference
HSiCl_3	$\text{H}(\text{CH}_2\text{CH}_2)_x\text{SiCl}_3$	1-5	[1]
$\text{HSiCl}_2\text{CH}_3$	$\text{H}(\text{CH}_2\text{CH}_2)_x\text{SiCl}_2\text{CH}_3$	1-6	[2]
$\text{HSi}(\text{C}_2\text{H}_5)_3$	$\text{H}(\text{CH}_2\text{CH}_2)_x\text{Si}(\text{C}_2\text{H}_5)_3$	1-2	[3]
$\text{HSiCl}_2\text{C}_6\text{H}_5$	$\text{H}(\text{CH}_2\text{CH}_2)_x\text{SiCl}_2\text{C}_6\text{H}_5$	1-3	[3]
$\text{HSi}(\text{C}_6\text{H}_5)_3$	$\text{H}(\text{CH}_2\text{CH}_2)_x\text{Si}(\text{C}_6\text{H}_5)_3$	1-2	[4]

TABLE 2. Constants for Trimethylalkylsilanes

Formula	$B, P., ^\circ\text{C}$			n_D^{20}		d_4^{20}		MR	
	observed	pressure	lit.* data	found	lit.* data	found	lit.* data	found	calc.
$(\text{CH}_3)_3\text{SiC}_2\text{H}_6$	61-62	760 <i>mm</i>	62	1,3831	1,3828	0,6906	0,6849	34,53	34,79
$(\text{CH}_3)_3\text{SiC}_4\text{H}_{10}$	115	"	115	1,4040	1,4040	0,7227	0,7203	44,08	44,14
$(\text{CH}_3)_3\text{SiC}_6\text{H}_{14}$	163	"	163	1,4172	1,4160	0,7450	0,7412	53,44	53,35
$(\text{CH}_3)_3\text{SiC}_8\text{H}_{18}$	200-202	"	202	1,4276	1,4242	0,7646	0,7646	62,62	62,58
$(\text{CH}_3)_3\text{SiC}_{12}\text{H}_{26}$	70-74	1 <i>mm</i>	273	1,4350	1,4358	0,7805	0,7800	80,04	80,47
$(\text{CH}_3)_3\text{SiC}_{14}\text{H}_{30}$	108-110	1 <i>mm</i>	300	1,4420	1,4410	0,7931	0,7911	90,26	90,61
$(\text{CH}_3)_3\text{SiC}_{16}\text{H}_{34}$	152-156	2 <i>mm</i>	—	1,4490	—	0,8061	—	99,72	99,91

*Literature data for dimethyl-n-alkylsilanes (see [5]) were determined at atmospheric pressure.

In this investigation we studied the thermal telomerization of ethylene with methylchlorosilane and with triethyl silane in greater detail. The methylalkyldichlorosilanes were obtained by methylation with Grignard reagent; thus individual silanes of structure $(\text{CH}_3)_3\text{SiC}_n\text{H}_{2n+1}$, for which $n = 1-16$ (only even members of this series)

TABLE 3. Analyses for Trimethylalkylsilanes

Formula	C, %		H, %		Si, %	
	found	calc.	found	calc.	found	calc.
(CH ₃) ₃ SiC ₁₂ H ₂₆	73,79 73,78	74,30	14,12 13,91	14,13	11,24 11,36	11,82
(CH ₃) ₃ SiC ₁₄ H ₂₉	75,14 75,58	75,47	13,75 14,03	14,15	10,04 10,12	10,37
(CH ₃) ₃ SiC ₁₆ H ₃₃	76,87 77,24	76,36	14,15 14,26	14,17		

TABLE 4. Fractions Obtained by Distillation of Products from Telomerization of Ethylene with Triethylsilane*

Fraction	Boiling point °C	p, mm Hg	Wt., g	Probable formula
I	108—109	(760)	164	(C ₂ H ₅) ₃ SiH
II	153	(760)	32	(C ₂ H ₅) ₄ Si
III	192	(760)	45,5	(C ₂ H ₅) ₃ SiC ₄ H ₉
IV	70—80	(2)	24,5	(C ₂ H ₅) ₃ SiC ₆ H ₁₃
V	80—96	(2)	31	(C ₂ H ₅) ₃ SiC ₈ H ₁₇
VI	96—104	(1)	18	(C ₂ H ₅) ₃ SiC ₁₀ H ₂₁
VII	104—114	(1)	10	(C ₂ H ₅) ₃ SiC ₁₂ H ₂₅
VIII	114—126	(1)	10,5	(C ₂ H ₅) ₃ SiC ₁₄ H ₂₉
IX	126—137	(1)	8	(C ₂ H ₅) ₃ SiC ₁₆ H ₃₃

* From the distillation of 466 g of reaction products obtained from 282 g of (C₂H₅)₂SiH.

were synthesized. The constants and analyses of the trimethylalkylsilanes obtained are given in Tables 2 and 3.

Telomerization of ethylene with triethylsilanes led to isolating silanes with the structure (C₂H₅)₃SiC_nH_{2n+1}. The reaction is conducted, as we described earlier [3], by heating the reaction mixture in an autoclave at 300° for 4 hr under an ethylene pressure of 250–300 atm. In Table 4 are given boiling points of the fractions obtained by distilling the reaction product, their probable composition, and weights for the yields of different telomers. Fractions II and III contain tetraethylsilane and triethylbutylsilane, which we described previously [3]. Fractions IV and V, containing triethylhexyl- and triethyloctylsilanes, are contaminated by close-boiling impurities and therefore it was not possible to obtain these telomer-homologs in pure form. In this study we succeeded in separating the individual triethyldecyl-, triethyldodecyl-, triethyltetradecyl- and triethylhexadecyl- silanes by repeated distillation of fractions VI–IX; their constants and analyses are given in Table 5.

For determining the structure of the aliphatic telomer chains we used the method suggested in the literature [6]. According to this method, the possibility is presented that measurements of intensity of the infrared absorption band in the region 2800–3000 cm⁻¹ is sufficiently reliable to determine the number of CH₂ and CH₃ groups in the aliphatic radical on the silicon atom. This possibility is based on the fact that linear increase in peak intensity corresponding to CH₂ and CH₃ groups is a measure of the number of these groups in the molecule. The influence of the Si atom on the intensity of adjoining methyl and ethyl groups is taken into account during the calculation.

This method allows us to distinguish between normal and branched chains, since the number of methyl groups increases in the presence of branching but the number of methylene groups decreases in comparison with the number of these groups in normal hydrocarbon radicals. The infrared spectra of the telomers was studied in CCl₄ solution in a cell of constant thickness and a LiF prism was used for large dispersion. The results obtained are given in Table 6.

As is seen in Table 6, for telomer-homologs in lines 1–6 and 10–11, complete correspondence between the number of CH₂- and CH₃- groups calculated for normal chains and found experimentally is observed; thus hydrocarbon chain branching does not occur in these cases. For telomer-homologs given in lines 7–9 and 12–15, ΔCH₂ and ΔCH₃ consistently increases with increasing chain length, but they have opposite signs, i.e., increase in the number of CH₃- groups is accompanied simultaneously by decrease in the number of CH₂- groups, and this must also occur with

TABLE 5. Results of Repeated Distillation of Fractions VI-IX

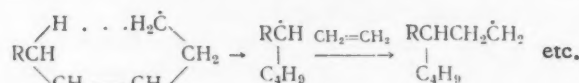
Formula	Boiling point, °C p mm Hg		n_D^{20}		d_4^{20}		MR		C, %		H, %		Si, %	
	observed	pres- sure	found	lit.* data	found	lit.* data	found	calc.	found	calc.	found	calc.	found	calc.
(C ₂ H ₅) ₃ SiC ₁₀ H ₂₁	101	(1)	1,4472	—	0,8047	0,8036*	85,34	85,62	74,62	74,91	13,99	14,15	10,60	10,94
(C ₂ H ₅) ₃ SiC ₁₂ H ₂₅	112—113	(1)	1,4560	—	0,8104	—	94,51	94,92	76,19	75,97	43,85	43,98	9,66	9,86
(C ₂ H ₅) ₃ SiC ₁₄ H ₂₉	125—126	(1)	1,4520	—	0,8132	—	103,67	104,22	76,30	76,84	44,00	43,99	9,76	8,63
(C ₂ H ₅) ₃ SiC ₁₄ H ₃₃	135—137	(1)	1,4539	—	0,8169	—	112,91	113,52	77,46	77,56	43,92	43,94	8,92	8,97
									77,60		44,13	44,21	8,14	8,235

* Literature data, see [5].

appearance of branched chains. It is necessary to mention that in the formation of a branch the number of CH₃-groups must be increased by one, but the number of CH₂- groups is decreased by 2. In Table 6 ΔCH_3 is actually near 1 for compounds 7-9 and 13-14 or equal to 2 (for compound 15). For 12 $\Delta\text{CH}_3 < 1$, which is due, obviously, to a mixture of inseparable isomers.

Examination of the data allows the assumption that formation of telomer homologs containing branched chains occurs under conditions for thermal telomerization of ethylene with silanes. Apparently this branching begins to play a substantial role for the higher telomers, beginning with C₁₂. Further examination of the data in Table 6 leads to the unexpected, on first glance, outcome that the sum of methyl, methylene, and methyne groups is less than the theoretical sum (of the number of carbon atoms) from the value of N_f. A negative value of N_f is found for branched chains but is not found with the normal ones. This phenomenon is connected to the fact that ΔCH_2 in Table 6 has an absolute value > 2 . Meanwhile, for one branching methyl group ΔCH_2 must be equal to 2. In the work cited [6] this phenomenon occurs (underestimating the CH₂ group absorption intensity) for a large number of hydrocarbons having $\ll T \gg$ -draped branching, for example, 4-propylheptane, 5-butylnonane, etc. In this connection it is possible to assume that the telomer homolog radicals studied, formed as a result of telomerization, have a T-shaped structure, i.e., the side chain of this radical has more than one carbon. It is possible that the rearrangement observed is analogous to the branching process in polyethylene obtained by radical polymerization of ethylene.

In this process [7] an intramolecular 1-5 shift of a hydrogen atom with formation of an n-butyl side chain in the polymer is proposed according to the scheme:



Study of IR-spectra of polyethylene obtained by radical polymerization of ethylene at high pressure showed that the number of CH₃- and C₂H₅- groups was equal in the samples studied. The authors interpreted this fact as evidence for the absence of side chains containing one carbon atom. Since with this view point a transition state through a three-membered ring is not very probable, the authors postulate that the side chains must contain 3-5 carbon atoms, but they assume formation of an n-butyl side chain [8] more probable. This assumption makes the idea that formation of T-shaped compounds during the thermal telomerization process and the idea that branching occurs only in the case of the higher telomers appear reasonable.

TABLE 6.* Number of Methyl and Methylene Groups in Telomers**

No. of expt.	Formula of telomer	No. of CH ₂ - group		Δ CH ₂	No. of CH ₃ - group		Δ CH ₃	Deficiency of C atoms	
		n _{theor}	n _{exptl}		n _{theor}	n _{exptl}		N _T	N _f
1	(CH ₃) ₃ Si ***)	—	—	—	4	4	0	0	0
2	(CH ₃) ₃ SiC ₂ H ₅	1	1	0	1	1	0	0	0
3	(CH ₃) ₃ SiC ₃ H ₇ ***)	2	2	0	1	1	0	0	0
4	(CH ₃) ₃ SiC ₄ H ₉	3	3	0	1	1	0	0	0
5	(CH ₃) ₃ SiC ₆ H ₁₃	5	5	0	1	1	0	0	0
6	(CH ₃) ₃ SiC ₈ H ₁₇	7	7	0	1	1	0	0	0
7	(CH ₃) ₃ SiC ₁₂ H ₂₄	11	8,3	-2,7	1	1,9	+0,9	-1,8	-0,9
8	(CH ₃) ₃ SiC ₁₄ H ₂₉	13	10,4	-2,6	1	2	+1	-1,6	-0,6
9	(CH ₃) ₃ SiC ₁₆ H ₃₂	15	12,2	-2,8	1	2,1	+1,1	-1,7	-0,6
10	(C ₂ H ₅) ₃ Si	1	1	0	1	1	0	0	0
11	(C ₂ H ₅) ₃ SiC ₄ H ₉	3	3	0	1	1	0	0	0
12	(C ₂ H ₅) ₃ SiC ₁₀ H ₂₁	9	7,8	-1,2	1	1,3	+0,3	-0,9	-0,6
13	(C ₂ H ₅) ₃ SiC ₁₂ H ₂₅	11	8,3	-2,7	1	2	+1	-1,7	-0,7
14	(C ₂ H ₅) ₃ SiC ₁₄ H ₂₉	13	9,5	-3,5	1	2	+1	-2,5	-1,5
15	(C ₂ H ₅) ₃ SiC ₁₆ H ₃₃	15	9,6	-5,4	1	3	+2	-3,4	-1,4

* n_{theor.} — calculated number of CH₂ and CH₃ groups for a telomer of normal chain structure; n_{expt.} — number of CH₂ and CH₃ groups found. $\Delta = n_{\text{exptl.}} - n_{\text{theor.}}$; N_T — difference between the number of carbon atoms in the chain, calculated from the formula and found spectroscopically from the number of CH₂ and CH₃ groups; N_f — the same value, but from the deduced number of methyl groups, apparently owing to branching. In the case of one secondary methyl group N_T must equal 1, but N_f is 0.

** Only CH₃ and CH₂ groups in the chains formed as a result of ethylene telomerization are considered, since (CH₃)₃Si and (C₂H₅)₃Si are subtracted earlier in the calculation.

*** These compounds were not obtained as a result of telomerization, but by an independent route, and are included in the table as standards to confirm the accuracy of the method used.

SUMMARY

1. Compounds of the general formula (CH₃)₃SiC_nH_{2n+1}, where n = 2, 4, 6, 8, 12, 14, 16, and (C₂H₅)₃SiC_nH_{2n+1}, where n = 2, 4, 10, 12, 14, 16 were obtained by a telomerization reaction.
2. The IR-spectra of the listed compounds, which showed the presence of branched chain next to the Si atoms, beginning with n = 10, were studied.
3. The assumption is expressed that the spectrally observed rearrangement of the alkyl group is observed as a result of telomerization by a process analogous to the branching of polyethylene, and leads to the formation of side chains containing more than one carbon atom.

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REACTION OF ALUMINUM CHLORIDE WITH DIALKYLCYCLOSILOXANES

A. A. Zhdanov, K. A. Andrianov, and A. A. Bogdanova

Institute for Heteroorganic Compounds, Academy of Sciences of the USSR

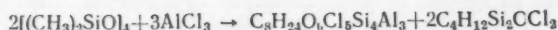
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

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Original article submitted September 26, 1960

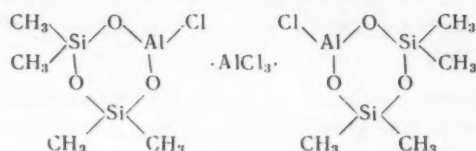
The reaction between dialkylcyclosiloxanes with aluminum chloride has not been described in the literature. The only exception is Hyde's patent [1], recorded in various countries, in which it is indicated that (in general) organocyclosiloxanes form dichloropolysiloxanes and crystalline compounds, possibly containing silicon and aluminum in their composition, upon reaction with aluminum chloride.

During a study of synthetic methods for polyaluminosiloxanes we became interested in studying the reaction of aluminum chloride with dimethyl- and diethylcyclosiloxanes. Study of the reaction established that aluminum chloride readily reacts with dimethyl- and diethylcyclosiloxanes in equimolar ratio and forms crystalline reaction products, which are quantitatively sublimed in vacuum. During study of reaction mixture compositions, obtained by the reaction of octamethylcyclotetrasiloxane with aluminum chloride, 1,3-di-chlorotetramethyldisiloxane boiling at 32-36° (10 mm), 1,5-dichlorohexamethyltrisiloxane boiling at 72-75° (10 mm), 1,7-dichlorooctamethyl-tetrasiloxane boiling at 90-95° (10 mm), and a crystalline substance of empirical formula $C_8H_{24}O_6Cl_5Si_4Al_3$ melting at 152-153° were separated from the reaction products. Such a reaction product could arise in the reaction mixture according to the scheme:



The crystalline substance with the empirical formula given above was shown to have constant composition by repeated sublimations and analytical studies. By alteration of the relative ratio of reacting components — octamethylcyclotetrasiloxane and aluminum chloride — the composition of the crystalline product was not changed. Study of its chemical properties showed that aluminum acetylacetonate was always formed upon reaction with sodium acetylacetonate; in this process only one of the three aluminum atoms present in the molecular composition formed acetylacetonate.

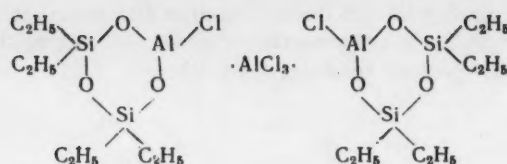
Analytical data and data from chemical studies allow the supposition that this crystalline substance contains a molecule of aluminum chloride bound in a complex and has the structure



The reaction of aluminum chloride with hexamethylcyclotrisiloxane proceeds similarly to octamethylcyclotetrasiloxane, but with this difference: besides the crystalline substance of composition $C_8H_{24}O_6Cl_5Si_4Al_3$, dimethyl-dichlorosilane and higher α, ω -dichloropolysiloxanes are formed. This process can be expressed by the following summary scheme:

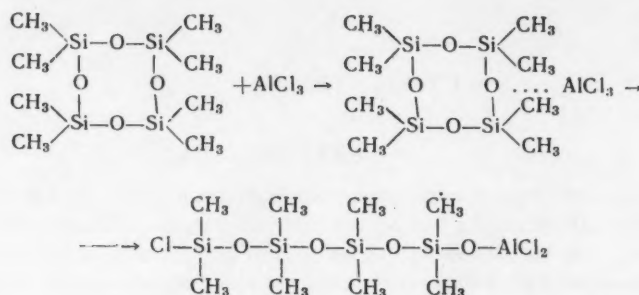


The analogous ethyl derivatives were separated by the reaction of aluminum chloride with octaethylcyclotetrasiloxane: 1,3-dichlorotetraethyl-disiloxane boiling at 85-90° (10 mm), 1,5-dichlorohexaethyltrisiloxane boiling at 124-131° (10 mm), 1,4-dichlorooctaethyltetrasiloxane boiling at 131-145° (10 mm), and a crystalline substance distilling at 225-233° (10 mm) and melting at 112° (unstable) of empirical formula $C_{16}H_{40}O_6Cl_5Si_4Al_3$ with analogous structure:

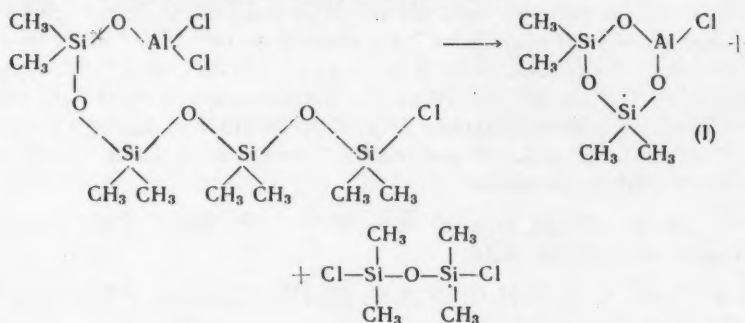


The identical crystalline substance of composition shown above, as well as diethyldichlorosilane and higher α, ω -dichloropolydiethylsiloxanes, was obtained by reaction of aluminum chloride with hexaethylcyclotrisiloxane.

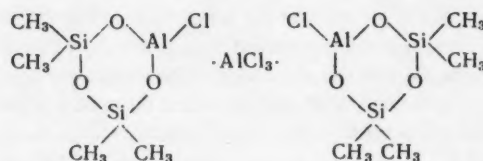
The data obtained experimentally allow presentation of the following idea about the reaction mechanism aluminum chloride with dialkylcyclotrisiloxanes; initially the aluminum chloride adds coordinately to an oxygen atom in the cyclic compound and 1-chloro-4-dichloroaluminooxyoctamethyltetrasiloxane is formed by subsequent ring opening.



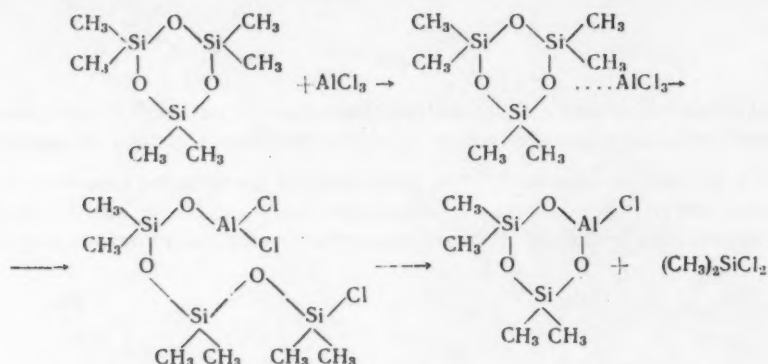
The 1-chloro-4-dichloroaluminooxyoctamethyltetrasiloxane being formed undergoes an intramolecular cyclization reaction with formation of a six-membered ring according to the scheme:



A side product at this stage of reaction is 1,3-dichlorotetramethyldisiloxane, which is capable in the presence of aluminum chloride in the reaction mixture of rearranging to higher α, ω -dichloropolysiloxanes. The formation of higher α, ω -dichloropolysiloxanes is explained by catalytic rearrangement of dialkylsiloxanes chains by the action of aluminum chloride. 1-Chloro-3,3,5,5-tetramethylcycloaluminooxysiloxane (I) formed during the reaction process yields a complex compound of the composition below in the presence of aluminum chloride:



This reaction mechanism agrees well with the experimental data and is confirmed by the reaction of aluminum chloride with hexamethylcyclotrisiloxane and hexaethylcyclotrisiloxane, where dimethyldichlorosilane and diethyldichlorosilane are formed as reaction products according to the scheme:



EXPERIMENTAL

Reaction of octamethylcyclotetrasiloxanes with aluminum chloride. In a flask with stirrer, reflux condenser and thermometer were placed 26.67 g (0.2 M) of aluminum chloride and 44.48 g (0.15 M) of octamethylcyclotetrasiloxane. The mixture was heated with stirring for 10 hr at 120° . A trap cooled by an acetone and dry ice mixture was placed at the condenser outlet during the ensuing vacuum distillation for the collection of any dimethyldichlorosilane possibly formed. At the end of reaction the trap was empty. The reaction products, consisting of a mixture of solids and liquids, were refractionated in vacuum. Thus were obtained 17.53 g of a fraction boiling $30\text{--}116^\circ$ (10 mm) and 34.24 g of a fraction boiling at $116\text{--}193^\circ$ (10 mm), which completely crystallized in the receiver. After a second careful fractionation and sublimation 28.12 g of white crystals melting at $152\text{--}153^\circ$, which sublimed easily under vacuum, was obtained. The substance dissolved well in alcohol (with heating) without evolution of hydrogen chloride, in water with formation of an oily layer, and in dry ether; in benzene it was soluble only upon heating. Found: C 16.63, 16.67; H 4.35, 4.28; Cl 29.92, 29.59; Si 20.24, 19.98; Al 12.55, 13.06%. $\text{C}_8\text{H}_{24}\text{O}_6\text{Cl}_5 \cdot \text{Si}_4\text{Al}_3$. Calculated: C 16.37; H 4.12; Cl 30.21; Si 19.14; Al 13.79%. The fraction boiling at $30\text{--}116^\circ$ (10 mm) was carefully refractionated a second time. Thus were separated fractions: I - b. p. $32\text{--}50^\circ$ (10 mm), 6.07 g (1,3-dichlorotetramethyldisiloxane); II - b. p. $50\text{--}75^\circ$ (10 mm), 5.73 g (1,5-dichlorohexamethyltrisiloxane), and III - b. p. $75\text{--}95^\circ$ (10 mm), 2.24 g (impure 1,7-dichlorooctamethyltetrasiloxane).

Fraction I - Found: Si 27.45, 27.56; Cl 33.09, 33.35%; d_4^{20} 1.0303, n_D^{20} 1.4103; MR 48.89. $\text{C}_4\text{H}_{12}\text{OCl}_2\text{Si}_2$. Calculated: Cl 34.90; Si 27.62; MR 48.18.

Fraction II - Found: Si 30.17, 30.48; Cl 25.86, 26.01%; d_4^{20} 1.0186; n_D^{20} 1.4071; MR 67.03. $\text{C}_6\text{H}_{18}\text{O}_2\text{Cl}_2\text{Si}_3$. Calculated: Cl 25.57; Si 30.36%; MR 66.82.

Fraction III - Found: Cl 22.93, 22.97; d_4^{20} 1.0142, n_D^{20} 1.4075; MR 85.39. $\text{C}_8\text{H}_{24}\text{O}_3\text{Cl}_2\text{Si}_4$. Calculated: Cl 20.18%; MR 85.46.

Reaction of octaethylcyclotetrasiloxane with aluminum chloride. The reaction was conducted in the same manner. Octaethylcyclotetrasiloxane (91.96 g; 0.225 M) and 40.00 g (0.3 M) of aluminum chloride were used for the reaction. The mixture was heated with stirring at 120° for 11 hr and then carefully fractionated under vacuum. As a result of fractional distillation the following fractions were collected: I - b. p. $85\text{--}90^\circ$ (10 mm), 21.13 g (1,3-dichlorotetraethylidisiloxane); II - b. p. $90\text{--}131^\circ$ (10 mm), 7.80 g (1,5-dichlorohexaethyltrisiloxane); III - b. p. $131\text{--}145^\circ$ (10 mm), 12.49 g (1,4-dichlorooctaethyltetrasiloxane); and IV - $225\text{--}233^\circ$ (10 mm) - a crystalline substance of composition indicated above in the amount of 27.85 g. The crystalline product obtained melted at 112° and was very hygroscopic, easily soluble in water with the formation of an oily layer, soluble in alcohol without evolution of hydrogen chloride, soluble in benzene and in ether. Found: C 27.23, 27.67; H 5.72, 5.71; Cl 25.49, 25.19; Si 16.21, 15.93; Al 10.82, 11.43%. $\text{C}_{16}\text{H}_{40}\text{O}_6\text{Cl}_5\text{Si}_4\text{Al}_3$. Calculated: C 27.49; H 5.77; Cl 25.36; Si 16.07; Al 11.58%.

The molecular weight of the substance determined cryoscopically in benzene was 657; 656. The calculated molecular weight is 699. If the high hygroscopicity of the substance is considered, it is possible to conclude that

the results obtained give good agreement with the calculated value. It is also necessary to point out that determination of the melting point of this substance was very difficult owing to its great hygroscopicity.

The low-boiling fractions separated were analyzed after purification; thus the following results were obtained:

Fraction I - Found: Si 20.84, 21.14; Cl 26.17, 26.46%; d_4^{20} 1.0203; n_D^{20} 1.4363; MR 66.48. $C_8H_{20}OCl_2Si_2$. Calculated: Cl 27.35; Si 21.64%; MR 66.70.

Fraction II - Found: Si 23.66, 23.19; Cl 19.02, 19.01%; d_4^{20} 1.0119; n_D^{20} 1.4393; MR 94.01. $C_{12}H_{30}OCl_2Si_3$. Calculated: Cl 19.62; Si 23.29%; MR 94.60.

Fraction III - Found: Si 24.24, 24.07; Cl 15.97, 15.02%; d_4^{20} 1.0063; n_D^{20} 1.4398; MR 121.38. $C_{16}H_{40}O_3Cl_2Si_4$. Calculated: Cl 15.30; Si 24.21%; MR 122.50.

Reaction of hexamethylcyclotrisiloxane with aluminum chloride. The reaction was conducted in the same manner. Hexamethylcyclotrisiloxane (44.48 g; 0.2 M) melting at 64° and 40.00 g (0.3 M) of aluminum chloride were used for the reaction. The reaction mixture was stirred for 6 hr at 50-60°, after which it was fractionally distilled. After fractional distillation the residue in the cold trap, cooled by a dry ice and acetone mixture, was 19.2 g of liquid, but 36.5 g of a substance which rapidly crystallized on cooling was distilled into the receiver at 180-182° (5 mm). By redistilling the volatile fraction four fractions were separated: I - b. p. 71-80°, 3 g; II - b. p. 80-90°, 4.1 g; III - 1.9 g in amount with boiling point 91-101°. All three fractions were impure dimethyldichlorosilane. Fraction IV (6.7 g, b. p. 101-144°) contained 37.72, 38.58% Cl and was 1,3-dichlorotetramethyldisiloxane containing admixed dimethyldichlorosilane. The crystalline substance melting at 153° was analyzed. Found: C 16.01, 16.07; H 4.10, 4.15; Cl 30.25, 30.25; Si 18.82, 18.75; Al 13.55, 13.51%. $C_8H_{24}O_6Cl_5Si_4Al_3$. Calculated: C 16.37; H 4.12; Cl 30.21; Si 19.14; Al 13.79%.

Reaction of hexaethylcyclotrisiloxane with aluminum chloride. The reaction was carried out in like manner. Hexaethylcyclotrisiloxane (61.30 g, 0.2 M) boiling at 100-104° (5 mm) and 40.00 g (0.3 M) of aluminum chloride were used. The mixture was stirred for 5 hr at 80°, after which it was fractionated under vacuum. After fractionation 5 g of a substance containing 36.22, 36.49% Cl and corresponding to impure diethyldichlorosilane (theoretical Cl content 45.14%) was collected in the cold trap. The high-boiling fraction collected at 83-86° (5 mm) weighed 14.2 g and contained 27.16; 27.16% Cl, and corresponded to 1,3-dichlorotetraethyldisiloxane (theoretical Cl content 27.35%). The crystalline fraction collected at 210-215° (5 mm) melted at 112° and was analyzed. Found: C 26.75, 26.63; H 5.68, 5.57; Cl 25.75, 25.95; Si 15.27, 15.30; Al 12.57, 11.98%. $C_{16}H_{40}O_6Cl_5Si_4Al_3$. Calculated: C 27.49; H 5.77; Cl 25.36; Si 16.07; Al 11.58%.

Reaction of sodium acetylacetonate with the complex from 1-chloro-3,3,5,5-tetramethylcycloaluminoxysiloxane and aluminum chloride. An alcoholic solution of sodium acetylacetonate was prepared from sodium ethoxide (4.6 g of sodium in 100 g of absolute alcohol) and 20 g of acetylacetone by the usual method. To the suspension of sodium acetylacetonate (containing 24.4 g of sodium acetylacetonate) (0.2 M) was added a solution of 24.24 g (0.04 M) of the crystalline complex in 100 ml of absolute alcohol. After 3 hr with stirring at 60°, 100 ml of benzene was added to the mixture; the sodium chloride formed was removed by filtration (11.25 g; yield 96.2% of theoretical) and the solvent was distilled from the filtrate. The residue obtained was treated with petroleum ether for removal of organosilicon derivatives, and the remaining residue was recrystallized from alcohol. There was obtained 11.8 g of pure aluminum acetylacetonate (91% of theoretical) melting at 913°. Found: C 55.65, 56.02; H 6.56, 6.79; Al 8.30, 8.35%. $C_{15}H_{21}O_6Al$. Calculated: C 55.55; H 6.53; Al 8.32%.

Reaction of sodium acetylacetonate with the complex from 1-chloro-3,3,5,5-tetraethylcycloaluminoxysiloxane and aluminum chloride. The reaction was carried out by an analogous method. Sodium acetylacetonate (15.87 g; 0.13 M) in 100 ml of alcohol and 19.80 g (0.026 M) of crystalline complex dissolved in 100 ml of alcohol were used for the reaction. Sodium chloride (7.7 g; 100% of theoretical amount) and 8.17 g of aluminum acetylacetonate melting at 193° (97% of theoretical amount) were obtained from the reaction.

SUMMARY

During the reaction between aluminum chloride and cyclic dialkylsiloxanes - octamethylcyclotetrasiloxane, octaethylcyclotetrasiloxane, hexamethylcyclotrisiloxane, and hexaethylcyclotrisiloxane - ring opening occurs with the formation of α -chloro- ω -dichloroaluminoxydialkylpolysiloxanes, which further split out α , ω -dichloropolysiloxanes and form cyclic compounds - 1-chloro-3,3,5,5-tetramethylcycloaluminoxysiloxane and 1-chloro-3,3,5,5-tetraethylcycloaluminoxysiloxane. These compounds were separated and characterized in the form of complexes with aluminum chloride.

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THE COHYDROLYSIS REACTION OF BIS-(METHYLDICHLORO-SILYL)BENZENE WITH TRIMETHYLCHLOROSILANE

K. A. Andrianov and N. V. Delazari

Institute for Heteroorganic Compounds, Academy of Sciences of the USSR

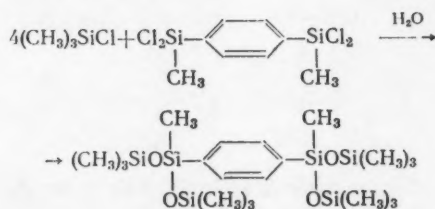
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

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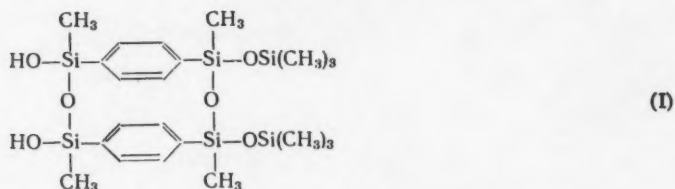
Original article submitted October 12, 1960

The hydrolysis reaction of monomeric organosilicon compounds containing phenyl groups and halogen on the silicon has not been studied. However compounds with this structure have a definite interest for synthesis of polymers with phenylenesiloxane groups in the molecular chains. The synthesis of linear compounds with phenylenesiloxane molecular chains has been described [1], as well as compounds containing bromine in the p-position on the phenyl [2].

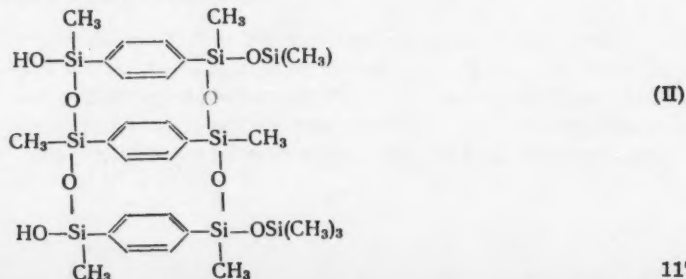
In this work attempts were made to study the cohydrolysis reaction of bis-(methylchlorosilyl)benzene, a monomer with tetrafunctionality, with trimethylchlorosilane. It was reasonable to expect that the cohydrolysis reaction with trimethylchlorosilane would occur according to the scheme:



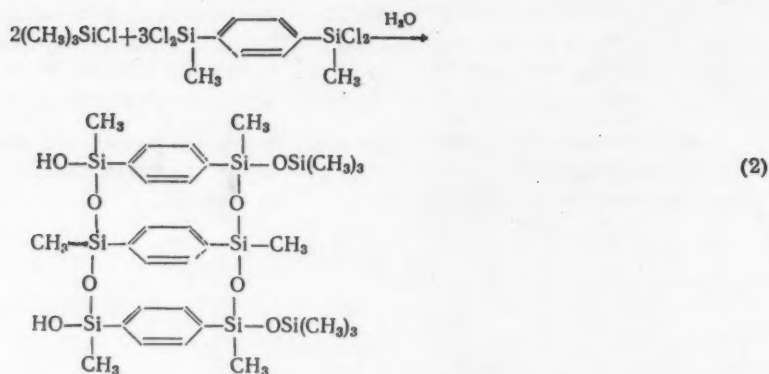
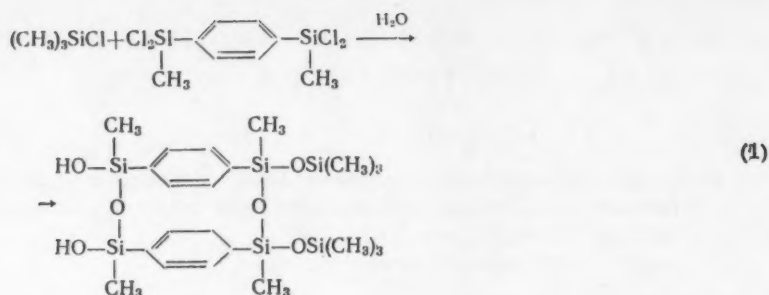
Investigation of the cohydrolysis reaction of bis-(methylchlorosilyl)benzene with trimethylchlorosilane in molar ratio 1:5 in dry ether medium and ammonia as [HCl] acceptor showed that the reaction does not go according to the given scheme, but products containing hydroxyl groups in their structure are always formed. These compounds were identified by elementary analysis data, hydroxyl group content, molecular weight determination, and infrared spectral data. One of the compounds isolated is a cyclic product, the structure of which corresponds to this formula:



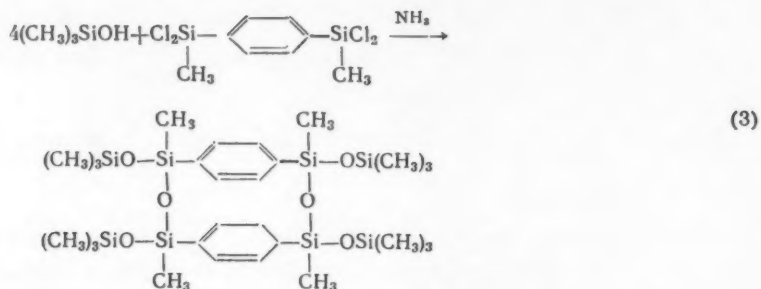
in which the position of groups was not established. Variation of reaction conditions toward increasing cohydrolysis time did not result in obtaining compounds lacking hydroxyl groups. Very complex products, containing hydroxyl groups which were formed as a result of further condensation reactions, were always isolated. In this case a compound with a bicyclic structure corresponding to formula (II) was separated.



Consequently, cohydrolysis of trimethylchlorosilane and bis-(methyldichlorosilyl)benzene occurs according to the reactions:



This shows that the cohydrolysis reaction of bis-(methyldichlorosilyl)benzene with trimethylchlorosilane occurs with great difficulty and under the described conditions, in spite of the large excess of trimethylchlorosilane, the latter takes part in the reaction only in molar ratios 1:1 or 1:1.5. These data show that the high rate for the hydrolysis of bis-(methyldichlorosilyl)benzene leads to initiation of the polycondensation reaction between the initial cohydrolysis products. The cyclic compound obtained is easily polymerized and converted to a high-polymeric substance. Complete replacement of chlorine in bis-(methyldichlorosilyl)benzene by trimethylhydroxysilyl groups can occur only by reaction with excess trimethylhydroxysilane on bis-(methyldichlorosilyl)benzene in the presence of ammonia according to the reaction:



EXPERIMENTAL

In a flask of 500 ml volume equipped with stirrer, thermometer, and dropping funnel were charged 24 ml of NH_4OH (15%), 100 g of ice, and 40 ml of ethyl ether. At a temperature of -8° a chloride mixture of 7.2 g (0.066 M) of trimethylchlorosilane and 5 g (0.0166 M) of bis-(methyldichlorosilyl)benzene was added. After addition of the chlorides there was no additional stirring. The ether layer was washed with water and dried over calcined Na_2SO_4 . The solvent was distilled; the starting material was distilled from the residue, which was dried to constant weight.

The substance obtained was a thick viscous liquid of yellow color; weight 3.83 g; 83.5% of theory. Found: C 46.10; H 7.29; Si 28.56; OH yield 5.46%; mole wt. 518. $C_{22}H_{40}Si_6O_6$. Calculated: C 46.48; H 7.04; Si 29.52; OH yield 5.97%; mol. wt. 568.

In a flask of 1 liter capacity equipped with stirrer, dropping funnel, and thermometer were placed 100 ml of NH_4OH (15%), 100 ml of ice water, and 200 ml of ethyl ether. At a temperature of -2° a mixture of 14.5 g (0.134 M) of trimethylchlorosilane and 10.1 g (0.033 M) of bis-(methyldichlorosilyl)benzene was added in drops. After addition of the chlorides stirring was continued for 30 minutes at the indicated temperature. The layers were separated at the end of the reaction. The ether layer was dried over calcined Na_2SO_4 . The solvent and starting material were distilled off. The residue was a very thick viscous liquid of yellow color; weight 7.47 g (88.6% of theoretical). Found: C 46.96; H 6.64; Si 29.89; OH yield 4.44%; mol. wt. 787. $C_{30}H_{50}Si_8O_8$. Calculated: C 47.24; H 6.57; Si 29.39; OH yield 4.46%; mol. wt. 762.

In a three-necked flask of 500 ml capacity were charged 300 ml of dry benzene and 19 g (0.211 M) of trimethylhydroxysilane. Bis-(methyldichlorosilyl)benzene (13.5 g; 0.447 M) in 50 ml of dry benzene was added in a stream of ammonia with cooling at -5° in ice. A white residue separated. After addition of the chloride, the ammonia flow was continued 30 minutes more; it was then left for 2 hr at the temperature of 30° for removing residual ammonia. The residue was filtered and the solvent evaporated. Upon distillation of the residue a fraction boiling $217-220^\circ$ (2 mm) was isolated; 2.2 g; 6.97% of theoretical; n_D^{20} 1.4610, d_4^{20} 0.9680; found MR 201.1; calculated MR 200.23. Found: C 46.95; H 8.78; Si 31.79%. $C_{28}H_{56}Si_8O_6$. Calculated: C 47.18; H 7.86; Si 31.46%.

SUMMARY

1. The cohydrolysis reaction of bis-(methyldichlorosilyl)benzene with trimethylchlorosilane proceeds with only partial replacement of halide by trimethylsiloxy groups.

2. Along with cohydrolysis, condensation of the hydrolysis products from bis-(methyldichlorosilyl)benzene occurs, leading to isolation of cyclic and bicyclic hydroxysilicon-containing compounds.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

STUDY OF THE EFFECT OF THE STRUCTURE OF UNSATURATED ORGANOSILICON COMPOUNDS ON THEIR HYDROGENATION RATES

L. Kh. Freidlin, I. F. Zhukova, and V. F. Mironov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

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Literature data indicated significant possibility of catalytic hydrogenation of ethylenic and acetylenic groups in organosilicon compounds. On a nickel catalyst substrate were hydrogenated under pressure: allyltrimethylsilane $(\text{CH}_3)_3\text{SiCH}_2\text{-CH=CH}_2$ [1], α -methylallyltriethylsilane $(\text{C}_2\text{H}_5)_3\text{SiCH(CH}_3\text{)-CH=CH}_2$, phenylsilanes $(\text{CH}_3)_4\text{-n-Si(C}_6\text{H}_5)_n$

(where $n=1,2,3,4$) [3], β -styryltrimethylsilane $(\text{CH}_3)_3\text{SiCH=CHC}_6\text{H}_5$ [4], γ -vinylxypropyltrimethylsilane $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OCH=CH}_2$ [5], 4-trimethylsilyl-2-methylbuten-3-ol-2 $(\text{CH}_3)_3\text{SiCH=CH-C(CH}_3)_2$ [6], and

bis-(2-methylbuten-1-yne-3)diethylsilane $(\text{CH}_2=\text{C(CH}_3\text{)-C}\equiv\text{C})_2\text{Si(C}_2\text{H}_5)_2$ [7] under normal pressure. Trimethylvinyl-


silane was hydrogenated on palladium oxide [8], but 1,1-dimethylsilylcyclopentene on Pt/C [9]. The triple bond in triethylvinylethynylsilane $(\text{C}_2\text{H}_5)_3\text{SiC}\equiv\text{C-CH=CH}_2$ was hydrogenated on palladium oxide as far as triethylbutylsilane, and also selectively to triethylbutadienylsilane or triethylbutenylsilane [10]. Pentyn-1-yltrimethylsilane $(\text{CH}_3)_3\text{SiC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$ on Pd-black or on platinum oxide added only one mole of hydrogen [11]. 4-Trimethylsilyl-2-methylbutyn-3-ol-2 on palladium also was hydrogenated only to the corresponding unsaturated alcohol. Complete hydrogenation was accomplished only on a nickel substrate [6]. The acetylenic disilane $(\text{C}_2\text{H}_5)_3\text{SiC}\equiv\text{CSi(C}_2\text{H}_5)_3$ was not hydrogenated on palladium oxide, but on nickel substrate under pressure only 10% of the saturated disilane was formed; the remaining 90% underwent decomposition [12]. We studied the influence of the length of carbon chain of the alkyl radicals (R) on the silicon atom and of the α , β , and γ -position of the double bond (relative to the silicon atom) on its hydrogenation rate. This rate and the stepwise character of ethynylsilane hydrogenation was also studied.

EXPERIMENTAL

The nickel catalyst substrate was prepared by leaching a Ni-Al alloy (1:1) with a 20% aqueous solution of sodium hydroxide and was stored under water. The catalyst was suspended in water on a torsion balance, washed with alcohol, and saturated with hydrogen. The reaction was conducted at 20° in 10 ml of 96% ethyl alcohol in a vessel, with vigorous stirring (700-800 rpm) with equimolar amounts of material. The reaction rate was characterized by the initial rate of hydrogen uptake (v_{init}) and by reaction half-life ($\tau/2$).

Hydrogenation of alkenylsilanes. In Table 1 are given the conditions and results for experiments in the study of the influence of alkenylsilane structure on hydrogenation rate of their double $\text{C}=\text{C}$ bonds. From Table 1 it is obvious that the volume of absorbed hydrogen is close to theoretical for the hydrogenation of all trialkylsilylalkenes. This verifies the purity of the substances used. In each case in which the amount of catalyst is doubled the reaction rate also approximately doubles. Replacement of two methyl groups by ethyl, n-propyl, or n-butyl has practically no influence on the hydrogenation rate (experiments 1-8). Increased substitution on the carbon atom of the $\text{C}=\text{C}$ double bond sharply reduces the hydrogenation rate (experiments 2 and 9; Fig. 1, curves 1 and 2). Study of the effect of the $\text{C}=\text{C}$ double bond position in compounds of the type $(\text{CH}_3)_3\text{Si(CH}_2)_n\text{CH=CH}_2$ in which $n = 0, 1$, or 2 showed that the hydrogenation rate for double bonds in the γ -position is greater than for the β -, but less than for α - (experiments 2, 11, 12 and 1, 10, Fig. 2). It is interesting to note that the reactivity of compounds in this homologous

TABLE 1

Expt. No.	Name and formula of hydrogenated compound	Constants of hydrogenated compounds			Used in reaction, g hydrogenated compound	In reaction, g catalyst	Hydrogen consumption, ml		Reaction rate	
		B.P., °C	n_D^{20}	d_4^{20}			theoretical	actual	ν , ml/15 sec	$\tau/2$, sec
1	Vinyltrimethylsilane (CH ₃) ₃ SiCH=CH ₂	54, 6	1, 3910	0, 6903	0, 2310	0, 2	51, 5	47, 5	15, 4	25
2	The same									
3	Vinyldiethylmethylsilane (C ₂ H ₅) ₂ CH ₂ SiCH=CH ₂	116, 6	1, 4225	0, 7504	0, 2310	0, 1	51, 5	49, 0	8, 5	50
4	The same				0, 2926	0, 2	51, 08	51, 1	15, 4	31
5	Vinyldipropylmethylsilane (n-C ₃ H ₇) ₂ CH ₂ SiCH=CH ₂	158, 0	1, 4330	0, 7664	0, 2926	0, 1	51, 08	51, 3	8, 5	47
6	The same				0, 3524	0, 2	50, 5	50, 5	16, 2	27
7	Vinyldibutylmethylsilane (n-C ₄ H ₉) ₂ CH ₂ SiCH=CH ₂	85, 0(15)	1, 4390	0, 7810	0, 3524	0, 1	50, 5	50, 4	8, 9	50
8	The same									
9	Propenyltrimethylsilane (CH ₃) ₃ SiCH=CHCH ₃	86, 0	1, 4081	0, 7167	0, 4186	0, 2	50, 8	50, 3	16, 1	29
10	Allyltrimethylsilane (CH ₃) ₃ SiCH ₂ -CH=CH ₂	85, 4	1, 4075	0, 7195	0, 4186	0, 1	50, 8	50, 3	8, 0	53
11	The same				0, 2578	0, 1	50, 5	47, 3	3, 0	230
12	γ -Butenyltrimethylsilane (CH ₃) ₃ SiCH ₂ CH ₂ CH=CH ₂	112, 0	1, 4148	0, 7358	0, 2652	0, 2	51, 0	47, 5	10, 6	41
13	Diallyldimethylsilane (CH ₃) ₂ SiCH ₂ -CH=CH ₂	135, 7	1, 4420	0, 7679	0, 2652	0, 1	51, 0	50, 0	4, 5	97
	(CH ₃) ₂ Si(CH ₂ -CH=CH ₂) ₂				, 2597	0, 1	45, 4	42, 4	5, 7	75
14	α -Cyclohexenyltrimethylsilane (CH ₃) ₃ Si 	171, 5	1, 4628	0, 8351	0, 1648	0, 1	52, 6	51, 9	5, 8	88
					0, 3721	0, 1	53, 5	—	0, 2	—

series decreases in this same order ($\alpha > \gamma > \beta$) toward radical polymerization reactions [13] and addition of chloroform, carbon tetrachloride, and aldehydes [14]. The addition of silane hydrides (HSiCl_3 and $\text{HSiCl}_2\text{CH}_3$) to vinylsilanes in the presence of platinum group catalysts also occurs markedly more rapidly than to allylsilanes [15]. In ionic addition reactions (halogens, hydrogen halides, thiocyanogen, thiocyanic acid) on the other hand, allylsilanes are more reactive, but vinylsilanes are less [16]; γ -butenylsilanes occupy an intermediate position. The hydrogenation rate of diallyldimethylsilane, in which molecule two double bonds occur, is approximately the same as allyltrimethylsilane (experiments 10 and 13).^{*} Thus it is possible to postulate that the double bonds of the diolefins are hydrogenated consecutively. The double bond in the cyclic molecule cyclohexenyltrimethylsilane adds hydrogen extremely slowly (experiment 14).

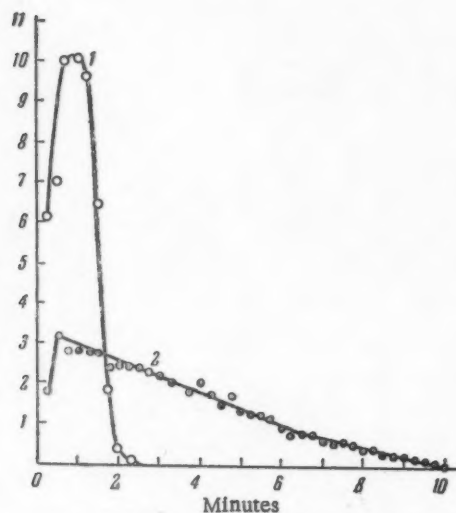


Fig. 1. Hydrogenation of vinyltrimethylsilane (1) and propenyltrimethylsilane (2).

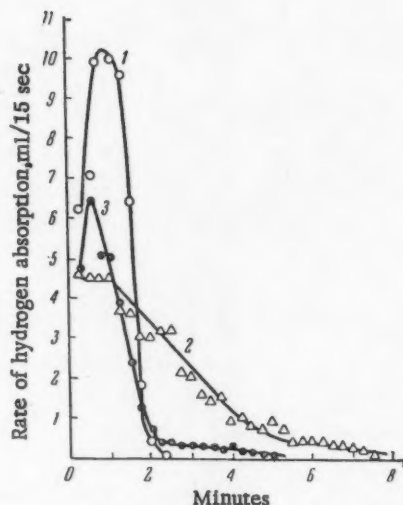


Fig. 2. Hydrogenation of vinyltrimethylsilane (1), allyltrimethylsilane (2), and butenyltrimethylsilane (3).

TABLE 2

Expt. No.	Name and formula of hydrogenated compound	Constants of hydrogenated compound			Amount of hydrogenated compound, g	Amount of pyridine (p) or quinoline (q) ml	Hydrogen consumption, ml		Reaction rate	
		temp. °C	n_D^{20}	d_4^{20}			theor.	actual	v_{init} ml/15 sec	$\tau/2$ in sec [*]
1	Ethyltrimethylsilylacetylene $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{SiC}\equiv\text{CH}$	83.2	1.4082	0.7435	0.1354	—	54.1	52.6	2.4	285
2	The same				0.1354	0.2 p	54.1	53.5	1.6	360
3	" "				0.1083	2.0	43.4	36.4**	0.7	615
4	bis-(Trimethylsilyl)acetylene $(\text{CH}_3)_2\text{SiC}\equiv\text{CSi}(\text{CH}_3)_2$	135.0	1.4260	0.7703	0.2210	—	58.7	55.8	0.4	1960
5	γ -Trimethylsilylpropargyl alcohol $(\text{CH}_3)_2\text{SiC}\equiv\text{CCH}_2\text{OH}$				0.1891	—	66.05	60.8	1.8	310
6	The same	65.0	1.4518	0.8753	0.1891	0.2 p	66.05	33.1	1.3	480
7	" "				0.1891	0.4 q	66.05	33.5	0.9	720

* Duration of absorption of first mole of hydrogen.

** Owing to the low rate, the reaction was not followed to the end.

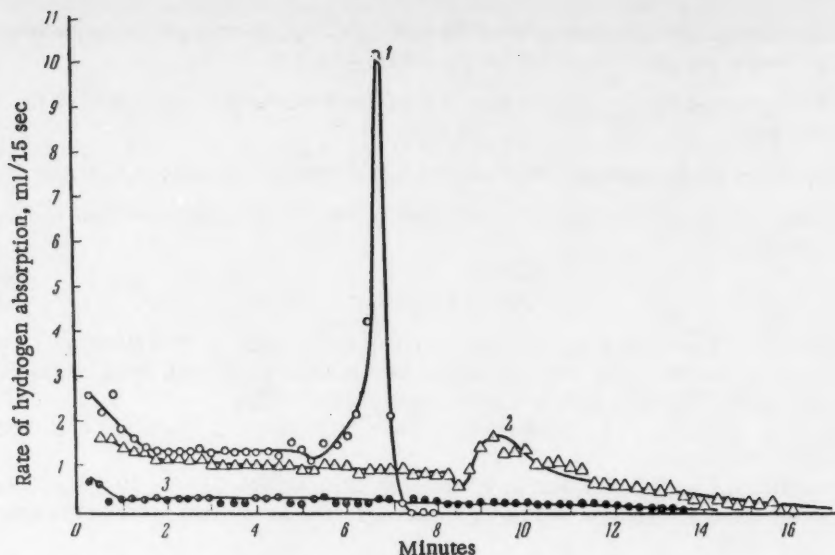


Fig. 3. Hydrogenation of ethyldimethylsilylacetylene (1); same in presence of pyridine (2); hydrogenation of bis-(trimethylsilyl)acetylene (3).

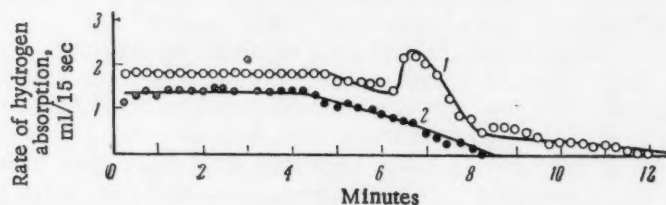


Fig. 4. Hydrogenation of trimethylsilylpropargyl alcohol (1); same in the presence of pyridine (2).

Hydrogenation of ethynylsilanes. The conditions and results of hydrogenation of mono- and disubstituted silylconacetylenes are given in Table 2. By comparison of initial rate and reaction half-lives (Tables 1 and 2) it is apparent that the triple bond in ethynylsilanes is hydrogenated markedly less rapidly than the double bond in alkenylsilanes. From Fig. 3 (curve 1) it is seen that initially ethyldimethylsilylacetylene is hydrogenated at a constant rate, which then sharply rises. The discontinuity in the curve corresponds to the absorption time for one mole of hydrogen, whereupon the rate for addition of the second mole of hydrogen is much greater than for the first. This points to the presence of two consecutive stages in the process; this stepwise character is confirmed by the fact that in the presence of small amounts of pyridine or quinoline the rate of absorption of the first mole of hydrogen is almost completely maintained, while the absorption rate for the second mole sharply decreases (Fig. 3, curve 2, experiments 2, 3).

Bis-(trimethylsilyl)acetylene, in which both hydrogens on the carbon atoms of the triple bond are replaced by trimethylsilyl radicals, is hydrogenated very slowly, while the reaction rate during the absorption of both the first and second mole of hydrogen remains constant (Fig. 3, curve 3, experiment 4). In the presence of pyridine this compound is not hydrogenated on nickel. In hydrogenation of γ -trimethylsilylpropargyl alcohol, in which both carbon atoms of the triple bond are substituted, a slight decrease in reaction rate during the second step is also observed (Fig. 4, curve 1, experiment 5). In the presence of pyridine or quinoline the maximum disappears; only one mole of hydrogen is absorbed. (Fig. 4, curve 2, experiments 6, 7). Evidently in the compounds cited the triple bond is hydrogenated consecutively: initially to a double, and finally to a single bond.

SUMMARY

1. The reactivity of olefinic compounds of the type $R_3Si(CH_2)_nCH=CH_2$ in hydrogenation on nickel depends on their position relative to the silicon atom and has the order: $\alpha > \gamma > \beta$.
2. The hydrogenation rate for a double bond in trialkylvinylsilanes does not depend on the length of the carbon chain in the alkyl group.
3. Ethynylsilanes are hydrogenated consecutively in two steps and markedly more slowly than alkenylsilanes.
4. Increasing the amount of substitution on the carbon atoms in the double and triple bonds sharply decreases their hydrogen addition rate.

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ORGANOSILICON COMPOUNDS WITH CARBON BRIDGES BETWEEN THE ATOMS OF SILICON

COMMUNICATION 2. THE INTERACTION WITH ALUMINUM HALIDES

V. M. Vdovin, K. S. Pushchevaya, and A. D. Petrov

The N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

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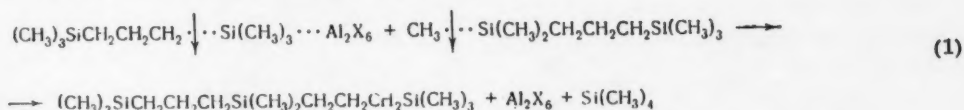
Original article submitted August 26, 1960

In the preceding communication [1], we reported on the polycondensation of 1,2-hexamethyldisilylthane which was observed by us, and which is specific for the chemistry of the organosilicon compounds. At the same time, two schemes for the mechanism of this transformation were suggested:

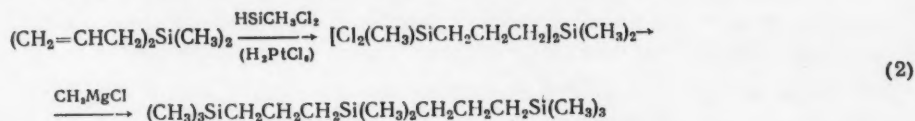
a) an intramolecular process occurring in the complex with Al_2X_6 $\text{CH}_3\cdots\downarrow\cdot\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\cdots\downarrow\cdot\text{Si}(\text{CH}_3)_3\cdots\text{Al}_2\text{X}_6$, as a result of which $\text{Si}(\text{CH}_3)_4$ and the biradical $[-\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2-]$ are formed; the latter is transformed into the cyclic polymers $[-\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2-]_n$.

b) an intermolecular process occurring between $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2$, $\text{Si}(\text{CH}_3)_2\cdots\downarrow\cdot(\text{CH}_3)$ and $\text{Zl}_2\text{X}_6\cdots(\text{CH}_3)_3\text{Si}\cdots\downarrow\cdot\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$, and leading to the formation of a linear dimer $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$ and to products of its further transformation. At that time, we isolated from the mixture of polymers only the cyclic products $[-(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2-]_n$, where $n = 2, 3$.

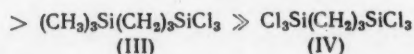
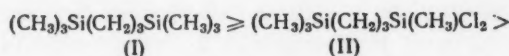
In the present work, we have investigated the behavior of 1,3-disilylpropane in an analogous reaction. The transformation proceeds here according to a scheme analogous to (b)



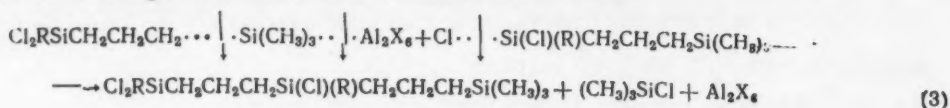
The dimer which is formed reacts further in similar fashion, giving principally linear polymers of the type $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2[\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2]_n\text{Si}(\text{CH}_3)_3$, where $n \geq 1$. The first two members of the series were isolated ($n = 1$ and 2); the structures of these were confirmed by their infrared spectra. The structure of the dimer was additionally confirmed by a second synthesis according to the scheme (2):



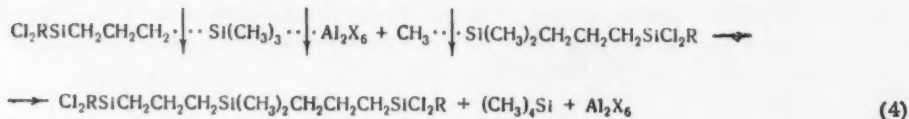
The properties of the substances obtained according to schemes (1) and (2) were identical. The cyclic dimer previously obtained by another reaction [2] was not observed. As a result of the investigation, the activities of the derivatives of 1,3-disilylpropane which contain different ratios of CH_3 - and Cl -groups at the Si atom are established to fall in the following (decreasing activity) series for the polycondensation reaction:



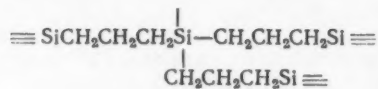
The last member of the series did not react in the presence of AlBr_3 taken in quantities up to 40 mole percent, even at a temperature of 200° . For the series members (II) and (III), judging from the low-boiling products of the reaction, the conversion proceeded according to schemes (3) and (4), which are similar to (b)



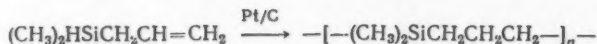
etc.,



The formation of $\text{Si}(\text{CH}_3)_4$ from the trichloride (III) indicates that the reaction proceeds via an intermolecular mechanism. In these experiments, there was formed in addition to the low boiling product a polymeric residue which contained hydrolyzable chlorine. When reaction (1) was carried out at a temperature below $90-100^\circ$, up to 0.95 M of $\text{Si}(\text{CH}_3)_4$ was isolated per mole of $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$, and there was formed a rubbery polymer of composition close to $[-\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2-]$ ($\text{SiC}_5\text{H}_{10}$). However, on further heating, especially in the presence of considerable quantities of the catalyst, the evolution of $\text{Si}(\text{CH}_3)_4$ began anew. We have suggested that the linear disilylpropane polymers which are formed undergo a structuration according to a scheme similar to (1) with a scission of the $\equiv\text{Si}\cdots\downarrow\cdots\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}\equiv$ bond. This reaction is accompanied by the formation of $\text{Si}(\text{CH}_3)_4$ and of a 3-dimensional polymer of the type:



In order to demonstrate the validity of our proposal we obtained a polymer of known linear structure by the method of [3]



and subjected it to heating with AlCl_3 . $\text{Si}(\text{CH}_3)_4$ was indeed evolved from the reaction mixture, and an insoluble three-dimensional polymer was formed.

Just as in the case of the derivatives of 1,2-disilylpropane, so, too, for the 1,3-disilylpropane derivatives, an increase of the mole percent of AlX_3 led to a decrease of the temperature at the beginning of the reaction. AlBr_3 was a more active catalyst than AlCl_3 .

The scissioning of the $\text{Si}-\text{C}$ bond of the disilylpropane group apparently takes place then when the compounds contain $\equiv\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}\equiv$ and $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ groups. Thus, in an attempt to split $[\text{Cl}(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{C}_2\text{H}_5)_2]\text{O}$ at the $\text{Si}-\text{O}-\text{Si}$ bond [4] by the action of AlX_3 , we did not succeed in isolating the α,ω -dichloride $\text{Cl}(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{Cl}$; a complex mixture of methyl- and ethyl-chlorosilanes with a b. p. less than 130° was formed in the reaction instead.

EXPERIMENTAL

The starting material, the disilylpropane compounds, were obtained according to known methods [5]; their properties were identical with those cited in the literature [5, 6]. The polymer $[-\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2-]_n$ was obtained according to the methods of [3] in the form of a viscous, colorless oil with b. p. greater than 300° .

The interaction of the 1,3-disilylpropane compounds with the aluminum halides was carried out in a flask with a downward inclined condenser and a trap for the low-boiling products (temperature 0 to -10°). The disilylpropanes were

used in 25-40 g quantities. A mixture of the disilylpropanes and AlX_3 was slowly heated on an oil bath. The temperature interval from the beginning of boiling to the appearance in the condenser of the vapors of the low boiling substance was taken to be the temperature of the beginning of the reaction. The low boiling substances which were formed were distilled out with Isooctane into a column of 20 theoretical plates and were identified by boiling point, n_D^{20} , and the infrared spectra. The polymeric residue was dissolved in benzene or ether. In the case of the polymer obtained from the $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_3$, the benzene solutions were treated with water for the decomposition of the catalyst; they were washed with a solution of soda, with water, and were dried over calcium chloride. After the removal of the solvent, the polymeric residue was analyzed. When the polycondensation reaction of 1,3-hexamethyldisilylpropane was carried out with the separation of greater than 0.95 M of $Si(CH_3)_4$ per mole of disilylpropane, the high molecular weight rubbery polymer which was formed was only partially soluble in benzene. Preparations of AlX_3 labeled chemically pure were used in the experiments. The use of sublimed $AlCl_3$ and the performance of the polycondensation of $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_3$ in an atmosphere of nitrogen led to an increase of the temperature of the beginning of the reaction. The results of the experiments are presented in the table.

1,3-Disilylpropane	AlX_3 , mole %	Temperature of the beginning of the reaction, °C	Temp. at the end of the reaction, °C	The product of the reaction in mole % of the initial material
$(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_3$	$AlCl_3$ (up to 5)	—	—	The starting material
The same	$AlCl_3$ (10)	80—90	95	$Si(CH_3)_4$ (93), Polymer
" "	$AlBr_3$ (5)	80—90	90	$Si(CH_3)_4$ (91), Polymer
$(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)Cl_2$	$AlBr_3$ (5)	145—180	**	**
The same	$AlBr_3$ (10)	80—90	180	$Si(CH_3)_4$ (7,5), $Si(CH_3)_3Cl$ (72), Polymer
" "	$AlCl_3$ (10)	115—140	**	**
$(CH_3)_3SiCH_2CH_2CH_2SiCl_3$	$AlBr_3$ (10)	120—130	220	$Si(CH_3)_4$ (22), $Si(CH_3)_3Cl$ (27), Polymer
$Cl_3SiCH_2CH_2CH_2SiCl_3$	$AlBr_3$ (up to 40)	—	—	The starting material

* The temperature of the reaction mixture; when the reaction did not occur, the mixture was boiled 3-5 min, and the starting material was distilled out.

** Was not determined.

The interaction of 1,3-hexamethyldisilylpropane with aluminum bromide. A mixture of 37.0 g (0.198 M) of the disilylpropane and 2.6 g (0.01 M) of $AlBr_3$ was heated on an oil bath in a flask with a good water condenser which communicated with the atmosphere through a trap cooled to -70° . At a temperature of $67-72^\circ$ a low boiling substance began to be formed. After 8 hr of boiling the temperature in the flask was lowered to 55° . On the following day the reflux condenser was replaced by an inclined condenser, and the low boiling substances which had been formed were distilled off on an oil bath heated to $70-85^\circ$ until 9.5 g of condensate had been collected; it consisted of $Si(CH_3)_4$. After the usual work-up of the heavy residue, the solvent was distilled away and the residue was distilled in vacuo. The following fractions were obtained: Fraction I, $65-67^\circ$ (18 mm), 7.0 g; Fraction II, 67° (18 mm) -120° (5 mm) mostly at $118-120^\circ$ (5 mm), 1 g; Fraction III, $122-124^\circ$ (5 mm), 5.0 g; Fraction IV, $123-180^\circ$ (2 mm) 3.8.

The undistilled residue was a viscous, light yellow oil weighing 7.0 g, $n_D^{20} = 1.4642$. The molecular weight of the residue (here and below, this was determined by the cryoscopic method in benzene) was 563. Found: C 60.08, 59.78; H 12.30, 12.12; Si 28.87%, 28.50. $Si(CH_3)_2CH_2CH_2CH_2$. Calculated: C 59.91; H 12.02; Si 28.02%.

Fraction I was the starting material itself, 1,3-hexamethyldisilylpropane $n_D^{20} 1.4220$, $d_4^{20} 0.7579$. Fractions II and III were the linear dimer $-(CH_3)_3SiCH_2CH_2[Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3]$; this substance redistilled completely at $88-91^\circ$ (3 mm); $n_D^{20} 1.4420$, $d_4^{20} 0.7970$; found MR 95.79; calculated MR 95.84; found mol wt. 295; calculated 288.

From Fraction IV by redistillation there was isolated what was probably the linear trimer $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2 \cdot$ $[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2]_2\text{Si}(\text{CH}_3)_3$ with b. p. 150–160° (2 mm); n_D^{20} 1.4521, d_4^{20} 0.8169; the molecular weight found was 372; calculated 389; found MR 128.4; calculated MR 128.6. Found: C 58.93, 58.76; H 12.09, 12.40; Si 29.10, 28.96%. $\text{C}_{19}\text{H}_{42}\text{Si}_4$. Calculated: C 58.67; H 12.44; Si 28.88%. The infrared spectrum confirmed the suggested structure of the substance.

The interaction of $[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2]_n$ with AlCl_3 . A mixture of 7 g of the polymer $[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2]_n$ and 1.5 g of AlCl_3 was heated at 120–200° in a boiling flask. The product of the reaction was 2.0 g of a low boiling substance, which from the data n_D^{20} 1.3610, d_4^{20} 0.6498 and the infrared spectrum was identified as $\text{Si}(\text{CH}_3)_4$. A dark solid substance remained in the flask.

The synthesis of $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2]_n\text{Si}(\text{CH}_3)_3$. An attempt was made to prepare diallyldimethylsilane from 1 M diallyldichlorosilane [7] by methylation with CH_3MgCl . The attempts were successful; the yield of diallyldimethylsilane was 52%. An attempt to methylate the dichloride with CH_3MgI was unsuccessful. Although in the latter case the reaction was carried out with the same ratios of the reagents and by analogous methods, at the decomposition stage of the reaction mixture with water in contrast to the successful experiment there was a vigorous evolution of propylene (identified as 1,2-dibromopropane); no diallyldimethylsilane at all was isolated; instead $[(\text{CH}_3)_2\text{SiO}]_3$ was obtained with b. p. 130–133° (atm); m. p. 62–63°, and $[(\text{CH}_2 = \text{CH}-\text{CH}_2)\text{Si}(\text{CH}_3)_2\text{O}]_n$ with b. p. 170–175°; n_D^{20} 1.4260, d_4^{20} 0.8250, as well as a considerable quantity of a polymeric substance.*

To 23 g of diallyldimethylsilane heated to 110° was added 2 drops of a 0.1 N solution of H_2PtCl_6 in isopropyl alcohol, followed by the drop-wise addition of 38 g of $\text{HSi}(\text{CH}_3)\text{Cl}_2$. When the temperature in the flask had reached 180° the mixture was cooled, and an additional 10 g of $\text{HSi}(\text{CH}_3)\text{Cl}_2$ was added; the contents of the flask were boiled for 2 hr. By distillation of the reaction mixture there was obtained 39 g of $[\text{Cl}_2(\text{CH}_3)\text{SiCH}_2\text{CH}_2\text{CH}_2]_2\text{Si}(\text{CH}_3)_2$ with b. p. 137–138° (2 mm); n_D^{20} 1.4720, d_4^{20} 1.0976. Found: Cl 38.3, 38.2%. $\text{C}_{10}\text{H}_{24}\text{Cl}_4\text{Si}_3$. Calculated: Cl 38.3%.

The tetrachloride obtained was methylated in the usual manner by the action of CH_3MgCl taken in a quantity double that calculated. $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2]_n\text{Si}(\text{CH}_3)_3$ was obtained in 68% yield; n_D^{20} 1.4420, d_4^{20} 0.7972. The infrared spectrum of this substance and of that obtained in Fractions II and III of the preceding experiment were identical.

The synthesis of α, ω -dichlorosilanes. Allyldimethylchlorosilane with b. p. 110° (756 mm); n_D^{20} 1.4295, d_4^{20} 0.9009 was obtained in 30% yield from 363 g of allyl bromide and 69 g of dimethyldichlorosilane by adding the mixture to 146 g of magnesium in 3 liters of ether. The symmetrical tetraalkyldihydrodisiloxanes were obtained according to the usual methods [8].

In a flask with a reflux condenser and a dropping funnel were placed 17.5 g of allyldimethylchlorosilane and 1 drop of a 0.1 N solution of H_2PtCl_6 in isopropyl alcohol, and the mixture was heated to boiling. Thereafter during 2 hr there was added dropwise $[\text{H}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{Si}]_2\text{O}$ (in all 10.5 g), after which the mixture was boiled for another 2 hr until the boiling point was 200°. After two successive distillations, 24 g of $[\text{ClSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{CH}_3)]_n(\text{C}_2\text{H}_5)_2\text{Si}]_2\text{O}$, 86% (based on the dichloride taken), was isolated with b. p. 146–147° (2 mm); n_D^{20} 1.4550, d_4^{20} 0.9560; found MR 122.4; calculated MR 122.7. Found: Cl 16.3, 17.0%; calculated: Cl 16.4%. In an analogous manner, from 2 molecules of allyldimethylchlorosilane and $\text{H}(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2\text{H}$ was obtained $[\text{ClSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2]_2\text{O}$ in 79% yield; b. p. 161–162° (8 mm); n_D^{20} 1.4482, d_4^{20} 0.9527; found MR 113.4; calculated MR 113.7. Found: Cl 17.6, 17.6%. Calculated: Cl 17.6%.

The α, ω -dichloride so obtained could be used for the synthesis of polymers with alternating α, ω -disilylpropane and siloxane fragments in the chain [9].

SUMMARY

1. Derivatives of 1,3-disilylpropane, in a manner similar to that of the 1,2-disilylethane compounds, undergo polycondensation with the separation of derivatives of monosilane and the formation of polymers with alternating atoms of Si and trimethylene fragments. The reaction occurs under the action of aluminum chloride and aluminum bromide.

* This curious splitting off of the $-\text{CH}_2\text{CH}=\text{CH}_2$ radical was observed also in the attempt to methylate $\text{CH}_2=\text{CHCH}_2\text{SiCl}_3$ with CH_3MgI , although in this case $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ was isolated in greater than 90% yield, and propylene was also violently evolved.

2. The application of this reaction to 1,3-hexamethyldisilylpropane yielded a mixture of polymeric homologs from which the linear dimer was isolated: $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$, the formation of which obviously occurred by intermolecular condensation between $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3 \dots \text{Al}_2\text{X}_6$ and $(\text{CH}_3)_3\text{SiCH}_2 \cdot \text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$.

3. In the interaction of the polymer $-\text{Si}(\text{CH}_3)_2-\text{CH}_2\text{CH}_2\text{CH}_2]_n-$ with AlCl_3 the possibility of a structural rearrangement of the linear polymers which contain α, ω -disilylalkane linkages into three-dimensional polymers was shown; this reaction also proceeds with the evolution of $\text{Si}(\text{CH}_3)_4$.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

THE MONOOXIDE AND DIOXIDE OF ABIETIC ACID

B. A. Arbuzov and A. G. Khismatullina

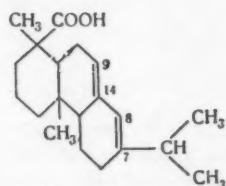
The V. I. Ul'yanov-Lenin State University of Kazan

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No. 7, pp. 1280-1287, July, 1961

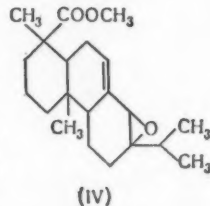
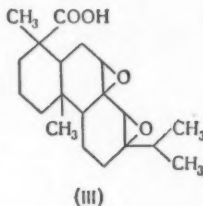
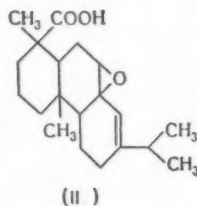
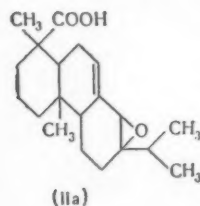
Original article submitted June 13, 1960

Abietic acid [1] has two double bonds which differ in their activities. The 7,8-bond is more easily reduced, the Di-n-amyamine salt of abietic acid is reduced with lithium and alcohol in ether or in liquid ammonia to 7,8-dihydroabietic acid [1]. The rates of oxidation of the double bonds of abietic acid with peracetic acids are different. One double bond oxidizes rapidly, the second considerably more slowly [2]. In an investigation of the ease of oxidation of the double bonds of abietic acid with peracetic acid, the products of the oxidation—the mono- and dioxides of abietic acid—were not isolated. In the present communication, we report on the separation of the monooxide and dioxide of abietic acid and on the structure of the monooxide.

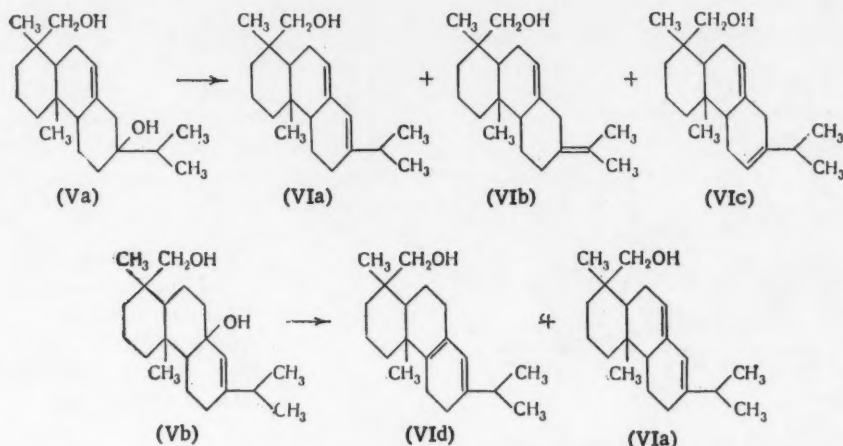


The monooxide of abietic acid was obtained by us by the oxidation of an ether solution of abietic acid with one equivalent of peracetic acid; it was purified by trituration with petroleum ether or through the morpholine or cyclohexylamine salts with subsequent separation from the salts with boric acid. The monooxide of abietic acid is a powdery substance with m. p. 94-96°; $[\alpha]_D = -7^\circ$ (in alcohol), the cyclohexylamine salt - m. p. 194-196°; $[\alpha]_D = -8^\circ$ (in alcohol), the morpholine salt - m. p. 108-111°; $[\alpha]_D = 0^\circ$ (in alcohol), the diacetoneamine salt - m. p. 75-78°; $[\alpha]_D = -2.1^\circ$ (in alcohol). The ultraviolet spectra of the original abietic acid, its monooxide and its cyclohexylamine salt are depicted in Fig. 1.

The dioxide of abietic acid (III) was obtained by oxidation of abietic acid with two equivalents of peracetic acid. Purified by treatment with petroleum ether or through the cyclohexylamine salt the dioxide was a powdery substance with m. p. 102-104°; $[\alpha]_D = 2^\circ$ (in alcohol), the cyclohexylamine salt - m. p. 204-208°; $[\alpha]_D = -2^\circ$ (in alcohol), the diacetoneamine salt - m. p. 95-97°; $[\alpha]_D = 0^\circ$ (in alcohol); the ultraviolet spectrum of the dioxide is given in Fig. 1. The spectra of the cyclohexylamine salt of the dioxide and of the morpholine salt of the monooxide are presented in Fig. 2. By the oxidation of methyl abietate with peracetic acid there was obtained the monooxide of the methyl ester of abietic acid (IV) with b. p. 154-158° (0.3 mm); $[\alpha]_D = -8.2^\circ$ (in alcohol); the ultraviolet spectra of methyl abietate and its monooxide are given in Fig. 3. If the structure of the dioxide of abietic acid (III) does not excite doubt, then for the monooxide there are two structures possible - (IIa) and (IIb). The determination of the structure of the monooxide presented the usual difficulties.



We selected the following path for the solution of this question. The reduction of the oxide ring with lithium aluminum hydride must lead in both cases (IIa) and (IIb), to a primary-tertiary glycol (Va) or (Vb). By reduction of the monooxide of abietic acid we obtained a glycol with m. p. 68-70°. $[\alpha]_D = -8^\circ$ (in alcohol). This same glycol (m. p. 67-69°) and $[\alpha]_D = -8.2^\circ$ (in alcohol) was obtained by reduction of the oxide of methyl abietate with LiAlH_4 . By the dehydration of the glycol, to which one can ascribe the structure (Va) or (Vb), one can expect the formation of unsaturated alcohols of different structures. If the glycol has the structure (Va), one would expect the formation of abietinol (VIa), the alcohol (VIb), or the alcohol with the unconjugated system of double bonds (VIc), or a mixture of all of them. If the glycol has the structure (Vb), dehydration could give abietinol (VIa) and palustrol (VId) with conjugated bonds.



In order to decrease the possibility of isomerization, the water elimination was carried out by vacuum distillation of the diacetate of the glycol at 200-206°; the latter was formed under conditions described for analogous systems by Kergomard [3]. The acetates of the diene alcohols were obtained, b. p. 198-220° (4 mm); $[\alpha]_D = -6^\circ$ (in alcohol). By acetylation of the glycol with acetic anhydride in acetic acid in the presence of sodium acetate with subsequent elimination of acetic acid by distillation, the acetates of the diene alcohols were obtained, b. p. 182-196° (3 mm); $[\alpha]_D = 10.5^\circ$ (in alcohol). The ultraviolet spectra of the acetates obtained by both methods are shown in Fig. 4. As is apparent from curves 2 and 3 of Fig. 4, the diene acetates so obtained possessed two maxima; these were at 242.5 $m\mu$ ($\alpha = 18$) and 250.0 $m\mu$ ($\alpha = 17$) from the experiment under Kergomard's conditions, and at 242.5 and 251.5 $m\mu$ ($\alpha = 21$) from the experiment using sodium acetate; in the latter case, the acetate with the absorption maximum at 242.5 $m\mu$ was present in a smaller quantity, and that with the absorption maximum at 251.5 $m\mu$ in a greater quantity than by the first method. The acetates with b. p. 198-220° (4 mm) were hydrolyzed with potassium hydroxide; the alcohols obtained after distillation possessed the b. p. 192-212° (2 mm); $[\alpha]_D = -2^\circ$ (in alcohol). Their ultraviolet spectra showed the same maxima at 240 $m\mu$ ($\alpha = 18.5$) and at 250.0 $m\mu$ ($\alpha = 17.5$) as the acetates (Fig. 5). The absorption maximum at 240.0 $m\mu$ corresponded to the maximum of abietinol; the maximum at 250.0 $m\mu$ was close to that of neoabietinol (251.0 $m\mu$; $\alpha = 88.3$) [4]. The abietinol obtained by us had the following constants: b. p. 182-184° (2 mm); $[\alpha]_D = -130^\circ$ (in alcohol); and absorption in the ultraviolet spectrum of 242.5 $m\mu$ ($\alpha = 80$). The magnitude of the absorption maximum at 242.5 $m\mu$ corresponded to a content of abietinol of 20-22%, the maximum at 251.0 $m\mu$, evaluated as neoabietinol, was approximately 20%. * The absorption spectra of the alcohols and their acetates showed the presence of alcohols without a conjugated system of double bonds.

In order to separate the alcohols with a conjugated system of double bonds from the alcohols without such a system, the alcoholic fraction was treated with maleic anhydride in benzene solution at 170-180°. From the products of the reaction a substance was separated in 18% yield with b. p. 80-82°; $[\alpha]_D = -5.5^\circ$ (in alcohol) which appeared to have the ester structure (VIII)

* Confirmation that the maximum at 250.0 $m\mu$ corresponds to neoabietinol, as it were, is given by the $[\alpha]_D = -6$, -8° of the alcohols prepared by Kergomard's method, and of +10, and +11 for the alcohols prepared with sodium acetate (abietinol $[\alpha]_D = -130^\circ$; neoabietinol, +184°); the maximum at 250.0 $m\mu$ in the second case is larger than in the first.

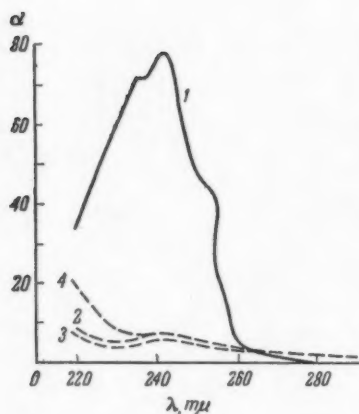
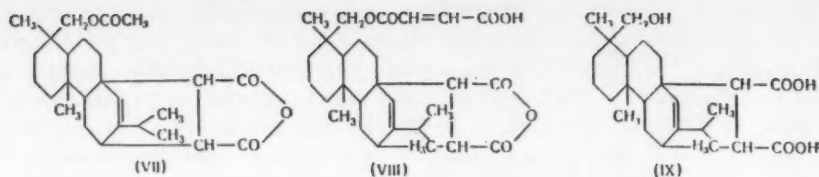


Fig. 1. The ultraviolet absorption spectra in alcohol of: 1) Abietic acid (I); 2) the monooxide of abietic acid (II); 3) the cyclohexylamine salt of the monooxide of abietic acid; 4) the dioxide of abietic acid (III).

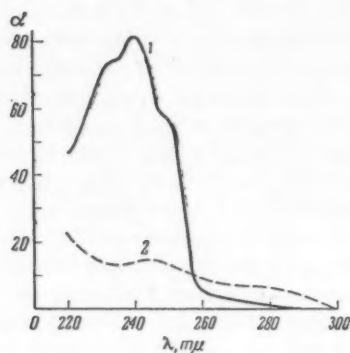


Fig. 3. The ultraviolet absorption spectra (in alcohol): 1) Methyl abietate; 2) monooxide of methyl abietate.

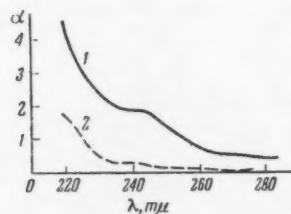


Fig. 2. The ultraviolet absorption spectra (in alcohol) of: 1) The morpholine salt of the monooxide of abietic acid; 2) the cyclohexylamine salt of the dioxide of abietic acid.

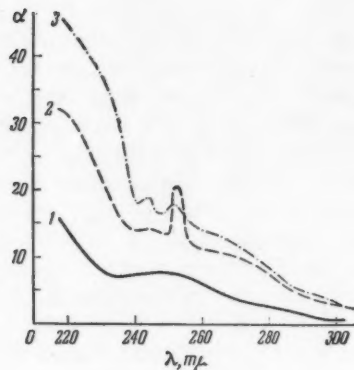


Fig. 4. The ultraviolet absorption spectra (in alcohol): 1) Glycol (VI); 2) acetates of diene alcohols obtained with use of CH_3COONa ; 3) acetates of diene alcohols by Kergomard's method.

is given as curve 1 for Fig. 6. After treatment of the original alcohols with hydrogen chloride for the isomerization of the diene alcohols (neobietinol) into abietinol, and subsequent treatment with an excess of maleic anhydride, the yield of the product (VIII) was 30%. Hydrolysis of the substance with m. p. 80-82° (VIII) gave the known dibasic hydroxy acid (IX) with m. p. 159-161°. The data from the literature [5]: m. p. 159-160°. The ultraviolet spectrum of (IX) is given in Fig. 6, curve 2. The same results were obtained by the action of an excess of maleic anhydride on the acetates of the diene alcohols which were obtained by the limination of acetic acid from the

This same product with m. p. 80-82° and $[\alpha]_D = -5.5^\circ$ (in alcohol) was obtained by a second synthesis from abietinol and excess of maleic anhydride. The ultraviolet spectrum

acetylated glycols (VII). In this case, the acetate of the anhydride (VII) with m. p. 114-117°; $[\alpha]_D = -16.1$ (in alcohol) was isolated; on hydrolysis, it gave the acid (IX) with m. p. 159-161°. The part of the alcohols which did not enter into the diene synthesis with maleic anhydride, but which was probably esterified by the excess of maleic anhydride melted at 30-50°; however it was impossible to purify this fraction by recrystallization or distillation in vacuo. The acetates of the alcohols (VI) were treated with maleic anhydride; the adduct with m. p. 114-117° (the

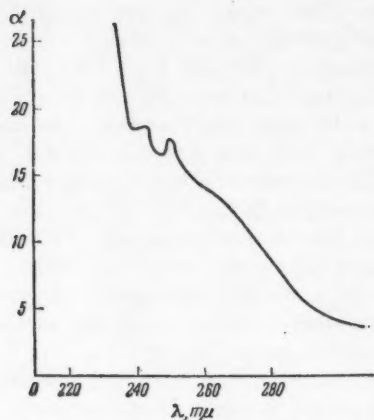


Fig. 5. The ultraviolet absorption spectra of alcohols (VII), obtained by hydrolysis of acetates of diene alcohols.

ultraviolet spectrum of this material is given in Fig. 7, curve 1) was removed, and the part which had not reacted with maleic anhydride was distilled in vacuo; the substance had b. p. 202-212° (3.5 mm); $[\alpha]_D = -3^\circ$ (in alcohol), and by analysis corresponded to the acetate of the diene alcohol (VI). The ultraviolet spectra of this fraction (202-212°/3.5 mm) is given as Fig. 7, curve 2. The absence of a maximum in the 240.0-270.0 m μ region shows that the double bonds in the acetate are not conjugated. Hydrolysis of the acetates gave alcohols with b. p. 196-202° (2.5 mm); $[\alpha]_D = -10.2$ (in alcohol). Their ultraviolet spectra are depicted by curve 3 in Fig. 7. The spectrum does not have a maximum corresponding to the presence of a conjugated system of double bonds. On the basis of the fact that the greater part of the alcohols (VI) do not contain a conjugated system of double bonds, one may conclude that the monooxide of abietic acid is the 7,8-oxide (IIa), since for the 14,9-oxide, the alcohols would contain a conjugated system of double bonds (VIa) and (VID).

EXPERIMENTAL

The monooxide of abietic acid. To an ether solution of 45 g of abietic acid [$m. p. 168-170^\circ$; $[\alpha]_D = -100^\circ$ in alcohol] cooled in ice was added with stirring a solution of 11.32 g of peracetic acid in 48 ml of ether. After 2 hr standing in ice, the solution was allowed to remain 4 hr at room temperature. The ether solution was washed with water and then dried over sodium sulfate; removal of the ether in vacuo left an oily substance which

was treated with petroleum ether while the glass surface was rubbed with a stirring rod. The monooxide of abietic acid was obtained in the form of a powder of m. p. 93-95°; $[\alpha]_D = -8.5^\circ$ (in alcohol). The yield was 36 g or 76% of the theoretical. Found: C 75.03; H 9.28%. $C_{20}H_{30}O_3$. Calculated: C 75.47; H 9.42%.

The cyclohexylamine salt of the monooxide, which was obtained by mixing acetone solutions of the monooxide and cyclohexylamine melted at 188-192°. After three recrystallizations from acetone, the melting point was 194-196°; $[\alpha]_D = -8^\circ$ (in alcohol). Found: N 3.04%. $C_{26}H_{43}O_3N$. Calculated: N 3.35%.

The morpholine salt was obtained analogously. The salt melted at 108-111° (from alcohol); $[\alpha]_D = \pm 0^\circ$ (in alcohol); it deliquesced in air. Found: N 3.05%. $C_{24}H_{39}O_4N$. Calculated: N 3.43%.

The diacetoneamine salt was obtained by bubbling ammonia through an acetone solution of the monooxide; m. p. 75-78° (from acetone); $[\alpha]_D = -2.1^\circ$ (in alcohol). Found: N 2.96%. $C_{26}H_{43}O_4N$. Calculated: N 3.23%.

The monooxide of abietic acid was separated with boric acid from the morpholine salt and had m. p. 94-96°; $[\alpha]_D = -7.5^\circ$ (in alcohol).

Preparation of the dioxide of abietic acid. To an ether solution of 5 g of abietic acid cooled in ice was added with stirring 5 g of peracetic acid (2 M) in 10 ml of ether. The solution was allowed to stand at room temperature for 15 days. A graph which represents the process of oxidation is given in Fig. 8. The subsequent treatment of the product was the same as for the monooxide. An 81.9% yield of the dioxide (4.5 g) was obtained with m. p. 100-103° (following treatment with petroleum ether and rubbing); $[\alpha]_D = -2^\circ$ (in alcohol). Found: C 71.48; H 8.92%. $C_{20}H_{30}O_4$. Calculated: C 71.86; H 8.98.

The cyclohexylamine salt of the dioxide was obtained in a manner analogous to that of the monooxide; m. p. 204-208° (from acetone); $[\alpha]_D = -3^\circ$ (in alcohol). Found: N 2.96%. $C_{26}H_{43}O_4N$. Calculated: N 3.23%.

The diacetoneamine salt melted at 95-97° (from acetone); $[\alpha]_D = \pm 0^\circ$ (in alcohol). Found: N 2.80%. $C_{26}H_{43}O_5N$. Calculated: N 3.05%. The dioxide of abietic acid, isolated from the cyclohexylamine salt with boric acid, had m. p. 102-104°; $[\alpha]_D = -2^\circ$ (in alcohol).

The preparation of the monooxide of methyl abietate. To an ether solution of 18.3 g of methyl abietate [b.p. 168-170° (0.5 mm)]; n_D^{20} 1.5344, d_4^{20} 1.047; the ultraviolet spectrum, maximum at 240.5 m μ ; (α = 81)] cooled in ice, an ether solution of 4.45 g of peracetic acid was added dropwise with stirring. The subsequent treatment was the same as for the monooxide of abietic acid. The yield was 15.6 g (80.4%) of the monooxide of methyl abietate with b. p. 154-158° (0.3 mm); $[\alpha]_D = -8.2$ (in alcohol). The ultraviolet spectra of methyl abietate and its monooxide are shown in Fig. 3. Found: C 75.52; H 9.70%. $C_{21}H_{32}O_3$. Calculated: C 75.90; H 9.63%.

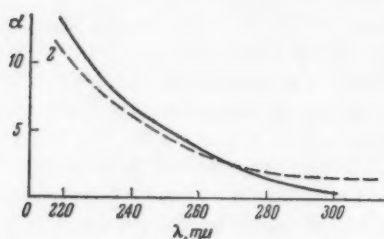


Fig. 6. The ultraviolet absorption spectra (in alcohol) of: 1) The adduct (VIII); 2) the dibasic hydroxy acid (IX).

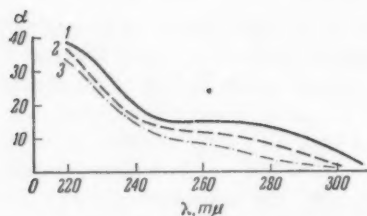


Fig. 7. The ultraviolet absorption spectra (in alcohol): 1) The adduct (VII); 2) the part of the acetate of the alcohols (VI) which did not react with maleic anhydride; 3) the part of the alcohol (VI) which did not react with molar anhydride.

b. p. 198-220° (4 mm); $[\alpha]_D = -6^\circ$ (in alcohol). The yield was 8.7 g or 80% of the theoretical. Found: C 79.58; H 10.26%. $C_{22}H_{34}O_2$. Calculated: C 80.00; H 10.30%.

The acetylation of the glycol with acetic anhydride in acetic acid. A mixture of 33 g of the glycol (V), 100 ml of acetic acid, 250 ml of acetic anhydride and 20 g of sodium acetate were heated for 3 hr at a moderate boil. The contents of the flask were then heated with distilled water on a water bath for an hour, after which they were dissolved in ether. The ether solution was washed several times with water, with a solution of soda, and with water again. The ether extract was dried over anhydrous sodium sulfate. Further treatment was as in the preceding experiment. The acetates were obtained with b. p. 182-196° (3 ml); $[\alpha]_D = +10.5^\circ$ (in alcohol). The ultraviolet spectra of the acetates are depicted in Fig. 4, curve 2. Found: C 79.62; H 10.34%. $C_{22}H_{34}O_2$. Calculated: C 80.00; H 10.30%.

The hydrolysis of the acetates of the diene alcohols. A mixture of 6 g of the acetates with b. p. 198-220 (4 mm); $[\alpha]_D = -6^\circ$ (in alcohol) and 3 g of potassium hydroxide in 100 ml of ethyl alcohol was heated; after 1 hr, 1 ml of water was added. After 2 hr heating the solution was acidified with 5% sulfuric acid and extracted with ether. The ether extract was washed with water and was dried over sodium sulfate for several days. Distillation gave a fraction of b. p. 192-212° (2 mm); $[\alpha]_D = -2^\circ$ (5 g or 92.3% of the theoretical). Found: C 82.96; H 11.04%. $C_{20}H_{32}O$. Calculated: C 83.33; H 11.11%. The ultraviolet spectrum of this fraction is depicted in Fig. 5.

The reduction of the monooxide of abietic acid with lithium aluminum hydride. An ether solution of 7.5 g of lithium aluminum hydride (a three-fold excess) was added dropwise and with energetic stirring to an ether solution of 20 g of the monooxide at such a rate that the ether solution was kept boiling. Following the addition, the flask was heated under reflux for 6 hr; on the following day the solution was poured into 400 ml of a 10% sulfuric acid solution. The ether layer was separated and washed with 10% sulfuric acid, with water, and with a 1% solution of KOH for the removal of the unreduced monooxide, and then again with water until no further basic reaction was obtained. The ether solution was dried over anhydrous sodium sulfate for several days, and then the ether was distilled away. The glycol (V) solidified after several days (m. p. 59-61°). The glycol was purified by trituration with petroleum ether on a porous plate, and melted at 68-70°; $[\alpha]_D = -8^\circ$ (in alcohol). Found: C 78.21; H 10.72%. $C_{20}H_{33}O_2$. Calculated: C 78.69; H 10.82%. The 2,4-dinitrobenzoate of the glycol, obtained by heating 2,4-dinitrobenzoyl chloride with the glycol, was crystallized from benzene-petroleum ether in the form of a fine powder and had m. p. 118-120°; $[\alpha]_D = -30^\circ$ (in chloroform).

The reduction of the monooxide of methyl abietate. The reduction of the monooxide of methyl abietate with lithium aluminum hydride was carried out under the same conditions as were used for the monooxide of abietic acid. The same glycol was obtained with m. p. 67-69°; $[\alpha]_D = -8.2^\circ$ (in alcohol). Found: C 78.26; H 10.75%. $C_{20}H_{33}O_2$. Calculated: C 78.69; H 10.82%.

The acetylation of the glycol and the elimination of acetic acid. The acetates were obtained by the method of Kergomard [3]. To 10 g of the glycol was added 50 ml of acetic anhydride. The flask was heated at 150-160° for 20 hr; it was then heated at 200-250°. Acetic acid was eliminated. The residue in the flask was distilled in vacuo;

The diene reaction of the alcohols with maleic anhydride. A benzene solution of 5 g of the alcohol fraction with b. p. 192-212° (2 mm) was mixed with a benzene solution of 2 g of maleic anhydride and heated in a sealed tube at 170-180° for 10 hr. After removal of the benzene and the excess maleic anhydride in vacuo, the residue was dissolved in ether. By dilution with petroleum ether, 1.55 g of a precipitate was obtained. After treating the precipitate with ether-petroleum ether three times, 1.1 g (18%) of a finely crystalline product (VIII) was obtained with m. p. 80-82°; $[\alpha]_D = -5.5^\circ$ (in alcohol). Found: C 69.74; H 7.32%. $C_{28}H_{36}O_7$. Calculated: C 69.42; H 7.41%. The residue from the separation of the product, with m. p. 80-82°, could not be distilled even at high vacuum. The yield of the product (VIII) was increased to 30% if the alcohol fraction was subjected to a preliminary isomerization by heating it in a benzene solution containing hydrogen chloride for 10-15 hr on a water bath.

The action of maleic anhydride on abietinol. Abietinol with b. p. 182-184° (2 mm); $[\alpha]_D = -130^\circ$ (in alcohol), the ultraviolet spectrum had a maximum at 242.5 m μ ($\alpha = 80$), was heated in benzene solution at 170-180° with an excess of maleic anhydride for 7 hr. The product obtained (VIII) melted at 80-82°; $[\alpha]_D = -5.5^\circ$ (in alcohol); 87% yield. The ultraviolet spectrum is depicted as curve 1 in Fig. 6.

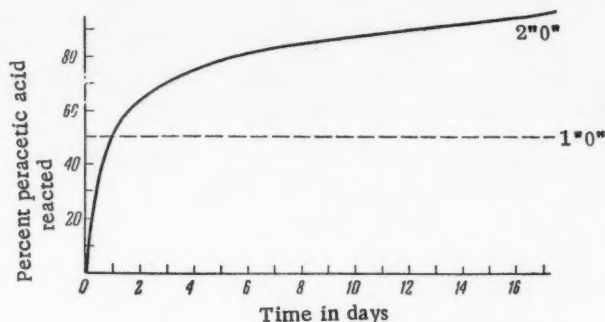


Fig. 8. Curve showing the oxidation of abietic acid by peracetic acid.

The hydrolysis of the product with m. p. 80-82°. The adduct (VIII), 1 g, in 70 ml of 0.1 M potassium hydroxide in methyl alcohol was heated for 30 min. After the addition of 1 ml of water, the mixture was again heated on a water bath for 6-7 hr; the contents of the flask were acidified by the addition of a solution of sulfuric acid; they were washed with water and extracted with ether. The ether extract was dried over sodium sulfate for several days. The residue, weighing 0.9 g after removal of the ether, was recrystallized from ether. A finely crystalline product weighing 0.7 g was obtained with m. p. 159-161°; $[\alpha]_D = -3^\circ$ (in alcohol). Literature data [5]: m. p. 159-160°. Found: C 70.96; H 9.00%. $C_{24}H_{36}O_5$. Calculated: C 71.28; H 8.91%.

The diene reaction of the acetate of the dienic alcohols with maleic anhydrides. A benzene solution of the acetates with b. p. 198-212° (4 mm); $[\alpha]_D = -3.6^\circ$ (in alcohol) and 1.5 g of maleic anhydride was heated in a sealed tube for 10 hr at 150-170°. After removal of the benzene and maleic anhydride in vacuo, the residue in the form of a grease was treated with a mixture of ether and petroleum ether. A yellow powder weighing 0.6 g was obtained with m. p. 86-93°. After numerous treatments of the residue with the mixture of ether and petroleum ether, there was obtained 0.4 g of the adduct with m. p. 114-117°; $[\alpha]_D = -16.1^\circ$ (in alcohol). Found: C 72.79; H 8.26%. $C_{26}H_{36}O_5$. Calculated: C 73.05; H 8.43%. The part of the acetates which had not reacted with the maleic anhydride was distilled in vacuo. A fraction was obtained with b. p. 202-212° (4 mm); $[\alpha]_D = -2^\circ$ (in alcohol). Found: C 79.62; H 10.12%. $C_{22}H_{34}O_2$. Calculated: C 80.00; H 10.30%. The ultraviolet spectrum of the adduct (VIII) is shown in Fig. 7, curve 1. The product with m. p. 114-117°, 0.3 g, was hydrolyzed with 15 ml of 0.1 N solution of potassium hydroxide in methyl alcohol by heating on a water bath for 30 min followed by the addition of 0.5 ml of water and further heating of the mixture for 4 hr. After acidification with 5% sulfuric acid, an ether extract was made which was washed with water, dried over sodium sulfate for several days, and yielded 0.2 g of a product with m. p. 159-161° (from ether); $[\alpha]_D = -3^\circ$ (in alcohol).

The hydrolysis of that part of the acetates which did not react with maleic anhydride. A mixture of 5 g of the part of the acetates which had not reacted with maleic anhydride and 150 ml of 0.1 N potassium hydroxide solution in methyl alcohol was heated on a water bath for 30 min. This was followed by the addition of 1 ml of water and

further heating for 4 hr, with subsequent treatment as in the preceding experiment; there was obtained 4 g of an alcohol with b. p. 196-202° (3 mm); $[\alpha]_D = -10^\circ$ (in alcohol). Found: C 82.91; H 11.04%. $C_{20}H_{32}O$. Calculated: C 83.33; H 11.11%. The ultraviolet spectrum of the alcohol is shown as curve 3 in Fig. 7.

SUMMARY

1. The monooxide and dioxide of abietic acid were obtained in pure form; the monooxide of methyl abietate was also obtained.
2. By reduction of the monooxide of abietic acid with lithium aluminum hydride the corresponding glycol was obtained. This same glycol was obtained by reduction of the monooxide of methyl abietate.
3. By elimination of acetic acid from the diacetate of the glycol there were obtained the acetates of the dienic alcohols; these consisted of acetates of alcohols with conjugated and with isolated systems of double bonds.
4. The presence of considerable quantities of alcohols with isolated double bonds showed that the original monooxide of abietic acid was the 7,8-oxide.

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ESTERS OF CYCLOHEXEN-2-YL-1-PHOSPHINIC ACID AND SOME OF THEIR DERIVATIVES

B. A. Arbuzov and E. N. Dianova

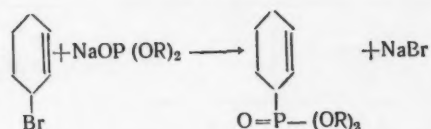
The A. M. Butlerov Chemical Institute and the V. I. Ul'yanov-Lenin
University of Kazan

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In the preceding report [1] we presented data on the synthesis of esters of cyclopenten-2-yl-1-phosphinic acid, and on the oxides produced from them by oxidation with peracetic acid. In developing these investigations we have carried out the syntheses of the analogous compounds with the 6-membered ring—the esters of cyclohexen-2-yl-1-phosphinic acid—and by their oxidation—the corresponding oxides. The diethyl ester of 1,2-epoxycyclohexyl-1-phosphinic acid was obtained earlier by Arbuzov, Vinogradova, and Plezhaeva [2] by the action of sodium diethylphosphite on α -chlorocyclohexanone. The esters of cyclohexen-2-yl-1-phosphinic acid are not described in the literature.

The dibutyl ester of cyclohexenylphosphinic acid was obtained earlier by Fay, and Lankelma [3] by the action of sodium dibutylphosphite on 3-bromocyclohexene-1. However, on hydrolysis of the ester with hydrochloric acid, they obtained cyclohexen-1-ylphosphinic acid. Thus, a displacement of the double bond had occurred either during the reaction of the bromide with the sodium dibutylphosphite or during the hydrolysis of the ester with hydrochloric acid. We synthesized the esters of cyclohexen-2-yl-1-phosphinic acid by the action of sodium dialkylphosphite on 3-bromocyclohexene-1



The physical constants of the esters are given in Table 1

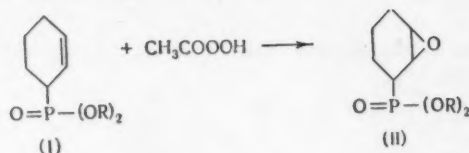
TABLE 1

R	B. p., °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR		P, %		Yield, %
				found	calcd.	found	calcd.	
CH ₃	92,5—93,5° (1,5)	1,4728	1,1386	47,94	47,34	—	—	11,0
C ₂ H ₅	93,5—94 (1)	1,4648	1,0690	56,42	56,58	14,43; 14,52	14,21	80,0
C ₃ H _{7-n}	119—120 (1)	1,4634	1,0262	66,16	65,82	12,68; 12,73	12,59	71,0
C ₃ H _{7-i}	107,5—108 (2)	1,4568	1,0203	65,73	65,82	12,64; 12,74	12,59	68,0
C ₄ H _{9-n}	129,5—130 (0,5)	1,4630	1,0082	74,95	75,05	11,30; 11,32	11,30	60,0
C ₄ H _{9-i}	133—134 (2)	1,4572	1,0015	74,64	75,05	11,66; 11,63	11,30	20,0

For proof of the structures of the esters which we had obtained, we ozonized the diethyl ester and oxidized the product of the ozonization with hydrogen peroxide under the conditions described by Fay and Lankelma [3]. A 27%

yield of glutaric acid was isolated from the product of these reactions in addition to succinic acid. The formation of the glutaric acid, in agreement with the data of the American authors, proves the structure of the ester to be the ester of cyclohexen-2-yl-1-phosphinic acid (I). The Raman spectra of the esters of cyclohexen-2-yl-1-phosphinic acid were measured. In the spectra were found the intense C=C frequency at 1648 cm^{-1} , the frequency of the valence vibration of the C-H group at a double bond at 3027 cm^{-1} , and of the P=O group at 1235 cm^{-1} .

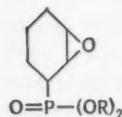
The esters of cyclohexenylphosphinic acid were easily oxidized by acetyl hydroperoxide with the formation of the esters of 1,2-epoxycyclohexyl-1-phosphinic acid (II).



The physical constants of the esters are given in Table 2.

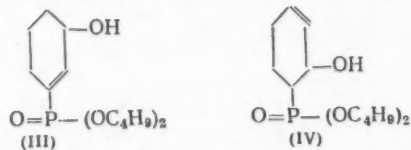
The Raman spectra of the esters of epoxycyclohexylphosphinic acid were also measured. In all of the spectra, a new line was found at 1273 cm^{-1} , not present in the spectra of the unsaturated esters, which can be related to the frequency of the valence vibration of the epoxy ring (an analogous frequency at 1255 cm^{-1} was found by us in the esters of 2,3-epoxycyclopentene-1-yl-1-phosphinic acid).

TABLE 2



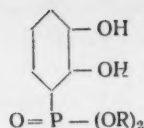
R	B. p., °C (p, mm Hg)	n_D^{20}	D_4^{20}	MR		P, %		Yield, %
				found	calcd.	found	calcd.	
C_6H_5	118,5—119 (1)	1,4633	1,1378	56,74	57,19	13,47; 13,56	13,24	86,0
$\text{C}_8\text{H}_{17-n}$	131—132 (1)	1,4618	1,0849	66,44	66,43	11,73; 11,68	11,82	88,0
$\text{C}_8\text{H}_{17-i}$	129—130 (2)	1,4561	1,0793	66,08	66,43	12,10; 12,17	11,82	87,0
C_4H_9-n	165—166 (0,5)	1,4650	1,0610	75,66	75,66	10,91; 10,88	10,68	53,4

The oxidation of the *n*-butyl ester of cyclohexen-2-yl-1-phosphinic acid yielded a higher fraction, in 23% yield, with the following constants: b. p. $182-183^\circ (0.5\text{ mm})$; n_D^{20} 1.4742, d_4^{20} 1.0644; found MR 76.70, $\text{C}_{14}\text{H}_{27}\text{PO}_4$ \equiv Calculated MR 76.58. Found: P 10.91, 10.83%. $\text{C}_{14}\text{H}_{27}\text{PO}_4$. Calculated: P 10.68%. The structures (III) or (IV) could be ascribed to this compound in analogy to the esters with the five-membered ring.



The esters of epoxycyclohexylphosphinic acid are easily hydrated in aqueous dioxane solution in the presence of hydrochloric acid with the formation of the esters of 2,3-dihydroxycyclohexyl-1-phosphinic acid. The constants of these substances are presented in Table 3.

TABLE 3



R	B.p., °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR		P, %		Yield, %
				found	calcd.	found	calcd.	
C ₂ H ₅	155—156 (1)	1,4788	1,4986	59,64	60,09	12,29; 12,01	12,29	90,6
C ₃ H _{7-n}	176—178 (1,5)	1,4743	1,1394	69,18	69,33	10,86; 10,83	11,06	71,0
C ₃ H _{7-i}	151—153 (1)	1,4678	1,1324	68,79	69,33	10,95; 10,76	11,06	81,0

EXPERIMENTAL

The interaction of 3-bromocyclohexene-1 with sodium diethylphosphite. To a solution 20,8 g of sodium diethylphosphite in dry ether was added 21 g of 3-bromocyclohexene-1 [4]. The flask was heated under reflux for 6 hr. After separation of sodium bromide (13,2 g) and removal of the ether, the residue was distilled in vacuo. The ethyl ester of cyclohexen-2-yl-1-phosphinic acid was obtained, 80% yield, 22,3 g, with b. p. 93,5–94° (1 mm).

The other esters of cyclohexenylphosphinic acid were obtained analogously.

The dimethyl ester. To a solution of 15,8 g of sodium dimethylphosphite in ether was added 19,3 g of 3-bromocyclohexene-1. The solution was refluxed for 10 hr. The yield of the ester was 2,5 g, b. p. 92,5–93,5° (1,5 mm).

The di-n-propyl ester. To 21 g of sodium dipropylphosphite in ether was added 18 g of 3-bromocyclohexene-1 and the solution was refluxed for 10 hr; the yield of the ester was 19,5 g, b. p. 119–120° (1 mm).

The di-n-butyl ester. From 27,8 g of sodium di-n-butylphosphite and 20,7 g of 3-bromocyclohexene-1 in ether solution was obtained 21 g of the n-butyl ester of cyclohexen-2-yl-1-phosphinic acid, b. p. 129,5–130° (0,5 mm).

The diisopropyl ester. From 25,7 g of sodium diisopropylphosphite and 22 g of 3-bromocyclohexene-1 in ether solution, by 16 hr heating on a water bath was obtained 22,8 g of the diisopropyl ester of cyclohexenylphosphinic acid, b. p. 107,5–108° (2 mm).

The diisobutyl ester. From 26,8 g of sodium diisobutylphosphite and 17 g of 3-bromocyclohexene-1 in ether there was obtained 5,7 g of the isobutyl ester of cyclohexen-2-yl-1-phosphinic acid, b. p. 133–134° (2 mm).

The oxidation of the diethyl ester of cyclohexen-2-yl-1-phosphinic acid with acetyl hydroperoxide. To a solution of 16,4 g of the diethyl ester of cyclohexen-2-yl-1-phosphinic acid in 30 ml of dry ether was added over a 30 min period a 100% excess of acetyl hydroperoxide (1 ml contained 0,08428 g of active oxygen). After 3 days, the reaction mixture was neutralized with an 8% solution of potassium hydroxide, and extracted with ether; the latter was then dried over potash sticks. After removal of the ether and distillation of the residue in vacuo, there was obtained 10,3 g (86%) of the diethyl ester of epoxycyclohexylphosphinic acid, b. p. 118,5–119° (1 mm).

Oxidation of the di-n-propyl ester of cyclohexen-2-yl-1-phosphinic acid. From 11 g of the di-n-propyl ester under the conditions described for the diethyl ester, there was obtained 10,3 g (88%) of the epoxy compound, b. p. 131–132° (1 mm). Similarly, from 16 g of the diisopropyl ester of cyclohexen-2-yl-1-phosphinic acid was obtained 14,8 g of the epoxy compound, b. p. 129–130° (2 mm).

The oxidation of the di-n-butyl ester of cyclohexen-2-yl-1-phosphinic acid. From 11 g of the dibutyl ester by treatment with a 100% excess of acetyl hydroperoxide, there was obtained 6,2 g (53,4%) of the di-n-butyl ester of epoxycyclohexylphosphinic acid. From the high boiling fraction was isolated 2,7 g (23%) of a product of b. p. 182–183° (0,5 mm); n_D^{20} 1,4742, d_4^{20} 1,0644; found MR 76,70; P 10,91, 10,83. C₁₄H₂₇PO₄ $\underline{\underline{L}}$. Calculated MR 76,58; P 10,68%.

The hydration of the dibutyl ester of epoxycyclohexylphosphinic acid. To a solution of 6 g of the substance in 15 ml of dioxane was added 5,5 ml of water and 1 ml of concentrated hydrochloric acid. On the next day after

removal of the water and dioxane, the residue was distilled. A 90.6% yield, 5.8 g, of the diethyl ester of 2,3-dihydroxycyclohexylphosphinic acid was isolated, b. p. 155-156° (1 mm). The hydration of the other esters of epoxy-cyclohexylphosphinic acid occurred under analogous conditions. The physical constants of the dihydroxy derivatives are given in Table 3.

The authors wish to express their appreciation of V. S. Vinogradova for the spectral determinations.

SUMMARY

1. Esters of cyclohexen-2-yl-1-phosphinic acid were synthesized by the action of sodium dialkylphosphite on 3-bromocyclohexene-1.
2. The corresponding oxides were obtained by oxidation with acetyl hydroperoxide.
3. The esters of 2,3-dihydroxycyclohexylphosphinic acid were obtained by hydration of the oxide.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SYNTHESIS OF β -AROYLACRYLIC ACIDS AND THEIR AMIDES

A. N. Nesmeyanov, N. I. Rybinskaya, and L. V. Rybin

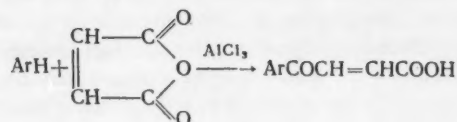
Institute of Heteroorganic Compounds, Academy of Sciences of the USSR

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No. 7, pp. 1292-1296, July, 1961

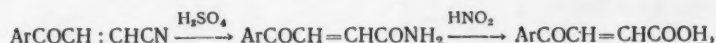
Original article submitted August 13, 1960

In the last decade there has been a notable increase of interest in the synthesis of β -aroylacrylic acids in connection with the possibility of their utilization as antibacterial and fungicidal agents [1, 2] and for the preparation of copolymers with other unsaturated compounds [3]. β -Aroylacrylic acids are prepared mainly by the reaction of maleic anhydride with aromatic compounds [1, 4]:



By taking suitable precautions, it is possible to obtain β -aroylacrylic acids monosubstituted in the para-position, as well as some polysubstituted derivatives. However, the method is not applicable either to the synthesis of the ortho-monosubstituted acids or acids with electronegative substituents. Two other synthetic methods are then employed, one of which consists in the dehydrobromination of the corresponding β -bromo- β -aroylpropionic acids [5, 6], and the other in the condensation of malonic acid with arylglyoxals [7]. All the remaining syntheses are of purely theoretical interest.

The present paper describes a new procedure which we have developed for the synthesis of β -aroylacrylic acids and their amides, by the hydrolysis of aryl- β -cyanovinyl ketones which can be obtained from β -chlorovinyl ketones [8]. Concentrated sulfuric acid hydrolyzes aryl- β -cyanovinyl ketones to the amides of the β -aroylacrylic acids, which can in turn be converted to the free acids by nitrous acid:

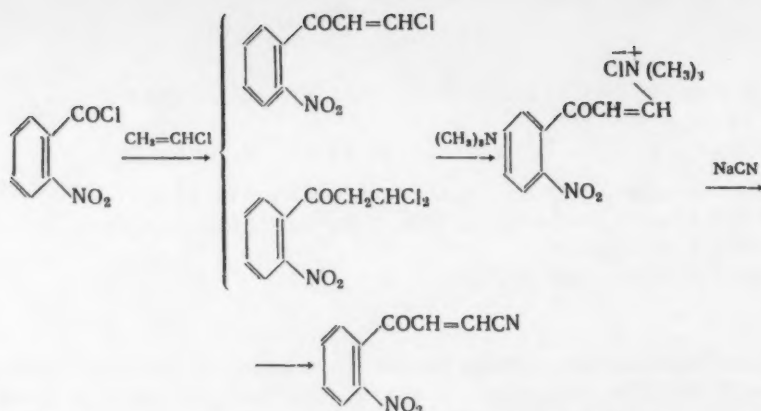


where $\text{Ar} = \text{C}_6\text{H}_5^-$; $\text{o-ClC}_6\text{H}_4^-$, $\text{o-BrC}_6\text{H}_4^-$, $\text{o-NO}_2\text{C}_6\text{H}_4^-$, $\text{p-BrC}_6\text{H}_4^-$. Lutz and Scott [9] converted the amide of β -(p-bromobenzoyl)acrylic acid, in moderate yield, into the free acid by the action of nitrous acid. We found that this conversion of the amides can be carried out in quantitative yield in a concentrated sulfuric acid solution using solid sodium nitrite and a lower temperature.

In the case of phenyl β -cyanovinyl ketone we were able to obtain β -benzoylacrylic acid directly (60% yield) by the action of a mixture of equal volumes of concentrated sulfuric and hydrochloric acids in a sealed tube at room temperature. Numerous attempts to hydrolyze aryl β -cyanovinyl ketones by other methods did not give the desired results.

The methods for the preparation of various ortho-substituted aroylacrylic acids developed in the present work made it possible to carry out a new synthesis of β -(o-nitrobenzoyl)acrylic acid, from which kynurenine can be readily obtained [5]. This natural product plays a major role in the genetically controlled formation of pigments in insects [10] and is the chief product of tryptophan metabolism in mammals and microorganisms [10, 11]. Kynurenine was first synthesized in 1942 by Butenandt and co-workers [12], who established its structure.

Butenandt's method, like others at present available [5, 13], involves very complex multistage synthesis, particularly as regards the preparation of the starting materials. We obtained β -(o-nitrobenzoyl)acrylic acid by the hydrolysis of its nitrile, which was synthesized as follows:



The most convenient syntheses of aryl β -chlorovinyl ketones are based on acetylene [14] and vinyl chloride [15]. In the case of *o*-nitrobenzoyl chloride the first method did not give the desired result. Vinyl chloride yielded a mixture of *o*-nitrophenyl β,β -dichloroethyl ketone and *o*-nitrophenyl β -chlorovinyl ketone. The mixture could be directly converted to β -(*o*-nitrobenzoyl)vinyltrimethylammonium chloride by treatment with an excess of trimethylamine. *o*-Nitrophenyl β -chlorovinyl ketone may be obtained from the mixture in a pure state by the action of the calculated quantity of trimethylamine necessary to split off the hydrogen chloride from *o*-nitrophenyl β,β -dichloroethyl ketone.

o-Nitro- β -cyanovinyl ketone was synthesized [8] from β -(*o*-nitrobenzoyl)vinyltrimethylammonium chloride. It was found that simultaneous addition of trimethylammonium chloride and sodium cyanide leads to a smoother reaction. β -(*o*-Nitrobenzoyl)acrylic acid, obtained by the hydrolysis of its nitrile, readily combines with ammonia to form β -(*o*-nitrobenzoyl)- α -aminopropionic acid. We adopted Butenandt's method [11] for the reduction of the NO_2 group in this acid since it ensures the greatest yield and purity of the desired product.

EXPERIMENTAL

Amides of β -Aroylacrylic Acids

Aryl β -cyanovinyl ketone (0.01 mole) was dissolved in 10 ml of concentrated sulfuric acid cooled in ice. After standing for two days in the refrigerator, the solution was poured out onto ice, and the precipitate was filtered off, washed with water, and dried (Table 1).

β -Acroylacrylic Acids

The amide (0.005 mole), prepared as described above, was dissolved in 6-10 ml of concentrated sulfuric acid. A 2.5- to 3-fold excess of solid sodium nitrite was then added to the solution cooled with solid carbon dioxide in acetone. Two to three ml of water was then gradually added and the mixture brought to room temperature. In the case of vigorous gas evolution the mixture was kept cold. After a further 15 ml of water had been added, the reaction mass was heated for 1-3 min on a 50-60° water bath; the precipitate was then filtered off, reprecipitated from 10% sodium carbonate solution with 10% hydrochloric acid, again filtered off, and dried (Table 2).

Hydrolysis of Phenyl β -Cyanovinyl Ketone to β -Benzoylacrylic Acid

Phenyl β -cyanovinyl ketone (0.6 g) was dissolved in 5 ml of concentrated sulfuric acid contained in a 100 ml glass ampoule; a test tube with 5 ml of concentrated hydrochloric acid was placed in the ampoule, which was then sealed off and the contents mixed. After two days, the reaction mixture was poured out onto ice. Before opening the ampoule, it is necessary to cool it in order to avoid loss of reaction mixture. The precipitate was filtered off and reprecipitated from sodium carbonate solution with hydrochloric acid. Yield 0.4 g of benzoylacrylic acid (60% of the theoretical); m. p. 96°. Published value [1]: 96°.

o-Nitrophenyl β -Chlorovinyl Ketone

Aluminum chloride [25 g (0.19 mole)] in 37 ml of nitromethane was added with constant stirring, over 1 hr, to 25 g (0.135 mole) of *o*-nitrobenzoyl chloride in 250 ml of dry dichloroethane, vinyl chloride being passed through at

TABLE 1

β -Aroylacrylic acid amide	Yield, %	M. p., °C	C, %		H, %		N, %		Halogen, %	
			found	calcd.	found	calcd.	found	calcd.	found	calcd.
$C_6H_5CCCH=CHCONH_2$	90	130 (recryst. from alcohol)	68,73	68,56	5,13	5,18	—	—	—	—
$o\text{-Cl(C}_6\text{H}_4\text{)COCH=CHCONH}_2\cdot H_2O^*$	94	126** (recryst. from aqueous alcohol)	52,69	52,76	4,48	4,43	6,17	6,15	—	—
$o\text{-NO}_2C_6H_4CH=CHCONH_2$	95	172 (recryst. from water)	54,28	54,55	3,61	3,67	12,76	12,73	—	—
$o\text{-BrC}_6H_4COCH=CHCONH_2$	90	199 (recryst. from water)	47,25	47,26	3,31	3,18	5,56	5,21	31,19	31,45
$p\text{-BrC}_6H_4COCH=CHCONH_2$	94	179-181*** (decomp., recryst. from alcohol)	—	—	—	—	—	—	—	—

* The melting point of the initial *o*-chlorophenyl β -cyanovinyl ketone was 66,5°. There was a misprint in Nesmeyanov and Rybinskaya's paper [8].

** Softens at 87-88°.

*** Published value [9]: m. p. 185° (decomp.).

TABLE 2

β -Aroylacrylic acid	Yield, %	M. p., °C	C, %		H, %		Halogen, %	
			found	calcd.	found	calcd.	found	calcd.
$C_6H_5COCH=CHCOOH$	96	96* (recryst. from toluene)	—	—	—	—	—	—
$o\text{-Cl(C}_6\text{H}_4\text{)COCH=CHCOOH}$	90	83 (recryst. from <i>n</i> -heptane)	57,03	57,02	3,45	3,35	16,83	16,83
$o\text{-NO}_2C_6H_4COCH=CHCOOH$	90	170** (recryst. from water)	54,23	54,31	3,29	3,19	—	—
$o\text{-BrC}_6H_4COCH=CHCOOH$	87	91,5 (recryst. from water)	47,23	47,09	2,85	2,77	31,24	31,33
$p\text{-BrC}_6H_4COCH=CHCOOH$	89	157***	—	—	—	—	—	—

* Published value [1]: m. p. 96°. There was no depression of the mixed melting point.

** Published value [7]: m. p. 173-173,5°.

*** Published value [4]: m. p. 159-160°.

the same time. The reaction mixture became hot and its color changed from pale yellow to violet. After the vinyl chloride had been passed through for 6 hr, the mixture was poured out onto ice acidified with hydrochloric acid. The dichloroethane layer was separated and the aqueous layer extracted several times with chloroform. The dichloroethane and chloroform extracts were refluxed with 2.5% sodium bicarbonate solution for 1½ hr and dried over CaCl₂; the solvents were then distilled off under a vacuum. The residue was recrystallized from petroleum ether; yield 15 g. According to analysis it is a mixture of *o*-nitrophenyl β,β -dichloroethyl ketone (60%) and *o*-nitrophenyl β -chlorovinyl ketone (40%). The latter may be obtained in a pure state by treating the mixture with the calculated quantity of triethylamine. Triethylamine (2.24 ml) in 20 ml of absolute ether was added dropwise to a solution of 7 g of a mixture of the mono- and dichloro-ketones in 50 ml of absolute ether cooled with ice. The precipitate formed after standing for 2 hr was filtered off and washed with absolute ether. The ethereal filtrate was then evaporated off and the residue dried; yield 5.8 g; m. p. 65° (recrystallized from petroleum ether). Yield *o*-nitrophenyl β -chlorovinyl ketone 44%, based on the initial acid chloride. Found: C 51.05; H 2.78; Cl 16.90; N 6.66%. C₉H₆ClNO₃. Calculated: C 51.08; H 2.86; Cl 16.76; N 6.62%.

o-Nitrophenyl β -Cyanovinyl Ketone

Dry ethylamine (25 ml) in 100 ml of absolute ether was added with vigorous stirring to a mixture of 5 g of *o*-nitrophenyl β -chlorovinyl ketone and *o*-nitrophenyl β,β -dichloroethyl ketone (prepared as described above) dissolved in 100 ml of absolute ether cooled with ice. After standing for 2 hr, the precipitate was filtered off, rapidly washed with absolute ether, transferred to a four-necked flask, and covered with 300 ml of ether. Solutions of 3 g of sodium cyanide in 10 ml of water and 5 g of trimethylammonium chloride in 10 ml of water were added with vigorous stirring, the latter somewhat faster, to the above mixture cooled with ice. The ethereal layer was then separated and another 200 ml of ether added. The latter operation was repeated twice more. The ethereal extracts were washed with water and dilute hydrochloric acid, and then dried over sodium sulfate. After the ether had been evaporated off, 3.52 g of *o*-nitrophenyl β -cyanovinyl ketone (70% of the theoretical) was obtained; m. p. 78° (recrystallized from *n*-heptane). Found: C 59.19; H 2.95; N 13.95%. C₁₀H₆N₂O₃. Calculated: C 59.41; H 2.99; N 13.86%.

The Hydrochloride of β -(*o*-Nitrobenzoyl)- α -Aminopropionic Acid

β -(*o*-Nitrobenzoyl)acrylic acid [1.32 g (0.006 mole)] was dissolved in 11 ml of 15% aqueous ammonia. After standing for 1 hr, the solution was evaporated to dryness and the residue dissolved in 6 N hydrochloric acid; the solution was then again evaporated to dryness and the residue washed with absolute acetone and dried. Yield 1.42 g (86% of the theoretical) of the hydrochlorides of β -(*o*-nitrobenzoyl)- α -aminopropionic acid; m. p. 185° (decomp.). Published value [5]: m. p. 186-187° (decomp.).

D,L-Kynurenine Sulfate

An aqueous solution of 0.5 g (0.0018 mole) of the hydrochloride of β -(*o*-nitrobenzoyl)- α -aminopropionic acid was hydrogenated over palladium black; 135 ml of hydrogen at 23° and 760.5 mm Hg was absorbed, which corresponds to 3 moles of hydrogen per mole of the hydrochloride. The palladium black was filtered off and washed with distilled water, the filtrate was acidified with 1.4 ml of concentrated sulfuric acid and evaporated, and the residue was treated with alcohol. The fine white needles, formed after standing for a short time in the refrigerator, were filtered off and dried in air. Kynurenine sulfate monohydrate was obtained in quantitative yield (0.58 g). Found: C 37.07; H 4.98; N 8.77%. C₁₀H₁₂N₂O₃ · H₂SO₄ · H₂O. Calculated: C 37.03; H 4.97; N 8.64%.

The ultraviolet absorption curve of the kynurenine sulfate obtained was identical with those given in the literature [11].

SUMMARY

1. Conditions for the hydrolysis of aryl β -cyanovinyl ketones to the corresponding β -aroylacrylic acids and their amides have been established.
2. The method of hydrolysis affords the normally difficult to obtain ortho-substituted β -aroylacrylic acids, in particular β -(*o*-nitrobenzoyl)acrylic acid, which can be converted to D,L-kynurenine.

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COMMUNICATION 2.* p-BIS(2-CHLOROETHYL)AMINO-D,L-PHENYL-
ALANYL-D,L-VALINE

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR
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$$(\text{ClCH}_2\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2-\underset{\text{NHR}}{\text{CH}}-\text{CO}-\text{NH}-\underset{\text{R}}{\text{CH}}-\text{COOC}_2\text{H}_5, \text{ (I)}$$
$$\text{(ClCH}_2\text{CH}_2\text{)}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2-\underset{\text{NH}\cdot\text{X}}{\text{CH}}-\text{CO}-\text{NH}-\underset{\text{R}}{\text{CH}}-\text{COOC}_2\text{H}_5, \text{ (II)}$$
$$\begin{aligned}
 & (\text{ClCH}_2\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2-\underset{\text{NHR}}{\text{CH}}-\text{COOH} + \text{NH}_2\underset{\text{COOCH}_2\text{Ph}}{\text{CH}}-\text{CH}(\text{CH}_3)_2 \longrightarrow \\
 & \longrightarrow (\text{ClCH}_2\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2-\underset{\text{NHR}}{\text{CH}}-\text{CO}-\text{NH}-\underset{\text{COOCH}_2\text{Ph}}{\text{CH}}-\text{CH}(\text{CH}_3)_2 \xrightarrow{\text{Pd}/\text{H}_2} \\
 & \longrightarrow (\text{ClCH}_2\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2-\underset{\text{NHR}}{\text{CH}}-\text{CO}-\text{NH}-\underset{\text{COOH}}{\text{CH}}-\text{CH}(\text{CH}_3)_2,
 \end{aligned}$$

1206

where R = CHO, CH₃CO; H. Sarcocylsyl-D,L-valine (IV) (R = H) was obtained by the deformylation, under mild conditions in the cold with alcoholic hydrogen chloride, of both N-formyl-D,L-sarcocylsyl-D,L-valine and its benzyl ester. In the latter case the dihydrochloride was subjected to the catalytic hydrogenolysis.

EXPERIMENTAL

(III) (R = CHO). A suspension of 7.42 g (0.023 mole) of N-formyl-D,L-sarcocylsine in chloroform was treated with 4.6 g (0.023 mole) of 1,3-dicyclohexylcarbodiimide and 4.64 g (0.023 mole) of the benzyl ester of D,L-valine; the mixture was vigorously stirred and left to stand overnight at room temperature. The resulting precipitate of 1,3-dicyclohexylurea was then filtered off and the filtrate evaporated in a vacuum; the residue was dissolved in a small quantity of ethyl acetate and completely reprecipitated with petroleum ether. The precipitate was then filtered off and twice recrystallized from ethyl alcohol. Yield 6.4 g (55%) of N-formyl-D,L-sarcocylsyl-D,L-valine benzyl ester; m. p. 110-112°. Found: C 59.98; H 6.36; Cl 13.87%. C₂₈H₃₃O₄N₃Cl₂. Calculated: C 59.76; H 6.36; Cl 13.57%.

(III) (R = COCH₃). This compound (m. p. 115-117°) was obtained in the same way from N-acetyl-D,L-sarcocylsine, in 45% yield. Found: C 59.96; H 6.54; Cl 13.3%. C₂₇H₃₅O₄N₃Cl₂. Calculated: C 60.38; H 6.56; Cl 13.21%.

(IV) (R = CHO). Compound (III) (R = CHO) (4.25 g) and 0.15 g of palladium black in 50 ml of methyl alcohol were shaken until absorption of hydrogen ceased. The catalyst was then filtered off, and the filtrate evacuated in a vacuum to a small volume, the resulting precipitate was filtered off and recrystallized from ethyl alcohol. Yield 3 g (86%) of N-formyl-D,L-sarcocylsyl-D,L-valine; m. p. 202-203°. Found: C 52.7; H 6.33; Cl 16.35%. C₁₉H₂₇O₄N₃Cl₂. Calculated: C 52.77; H 6.29; Cl 16.43%.

(IV) (R = COCH₃). This compound (m. p. 158°) was obtained as described above from (III) (R = COCH₃), in 78.5% yield. Found: C 53.75; H 6.64; Cl 15.43%. C₂₀H₂₉O₄N₃Cl₂. Calculated: C 53.80; H 6.55; Cl 15.89%.

(IV) (R = H). Compound (IV) (R = CHO) (1.5 g) was dissolved in 300 ml of 1% ethanolic hydrogen chloride and allowed to stand for 3 hr at room temperature. The alcohol was then distilled off in a vacuum to a very small volume, absolute ether was added until the precipitation was complete, and the mixture left to stand overnight in the refrigerator. The resulting pinkish precipitate was filtered off. Yield (almost quantitative) 1.68 g of D,L-sarcocylsyl-D,L-valine dihydrochloride, melting at 120° with intense decomposition and color change to red. Found: C 45.24; H 6.34; Cl 26.93; N 8.56%. C₁₈H₂₉O₃N₃Cl₄. Calculated: C 45.28; H 6.12; Cl 29.72; N 8.80%.

The dihydrochloride (0.92 g) was dissolved in 5 ml of ethanol and treated with a solution of 0.289 g of diethylamine in 3 ml of alcohol. The free base was precipitated by the addition of 5 ml of absolute ether, filtered off, and twice recrystallized from ethanol. Yield 0.4 g (51.65%) of D,L-sarcocylsyl-D,L-valine [(IV) (R = H)]; m. p. 225-226°. Found: C 53.45; H 6.80; Cl 17.22; N 10.51%. C₁₈H₂₇O₃N₃Cl₂. Calculated: C 53.47; H 6.73; Cl 17.54; N 10.39%.

The benzyl ester (III) (R = CHO) (0.2 g) was treated with alcoholic hydrogen chloride as described above. The resulting dihydrochloride of D,L-sarcocylsyl-D,L-valine benzyl ester and 0.05 g of palladium black were shaken in 45 ml of methyl alcohol until absorption of hydrogen ceased. The catalyst was filtered off, the filtrate evaporated in a vacuum, and the residue treated with absolute ether. Yield 0.15 g of the dihydrochloride of (IV) (R = H). HCl was removed as described above and the product recrystallized three times from ethanol. The D,L-sarcocylsyl-D,L-valine obtained melted at 224-226°. There was no depression in the melting point on fusion together with the peptide obtained by the previous method (mixed m. p. 224-226°).

SUMMARY

Peptides bearing the bis(2-chloroethyl)amino group were obtained by the catalytic hydrogenolysis of the corresponding benzyl esters.

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CARCINOLYTIC PEPTIDES WITH SELECTIVE ACTION

COMMUNICATION 3. N-[p-BIS(2-CHLOROETHYL)AMINOPHENYLACETYL]- AMINO-ACIDS AND N-(γ -[p-BIS(2-CHLOROETHYL)AMINOPHENYL]- BUTYRYL)AMINO-ACIDS

K. I. Karpavichus, N. E. Golubeva, O. V. Kil'disheva

and I. L. Knunyants

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR

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Biological tests on our earlier antitumor preparations — ethyl esters of amino-acids and peptides acylated with p-bis(2-chloroethyl)aminophenylacetic and γ -[p-bis(chloroethyl)aminophenyl]butyric acids [compounds of type (I) ($R' = C_2H_5$)] — have shown that they possess high antitumor activity. Unlike p-bis(2-chloroethyl)aminophenylacetic and γ -[p-bis(2-chloroethyl)aminophenyl]butyric acids themselves, they are non-toxic and exhibit considerable selectivity in their action on various types of carcinoma [1-7]. To elucidate the effect of the ester group (R') in peptides of type (I), we have prepared the benzyl and diethylaminoethyl esters of these peptides [(I) ($R' = CH_2Ph, CH_2CH_2N(C_2H_5)_2$)] (Table 1).

The esters were synthesized by the condensation of the amino-acid benzyl esters with p-bis(2-chloroethyl)aminophenylacetic and γ -[p-bis(2-chloroethyl)aminophenyl]butyric acids in the presence of 1,3-dicyclohexylcarbodiimide. The diethylaminoethyl ester of p-bis(2-chloroethyl)aminophenylacetyl-D,L-phenylalanine (compound 7, Table 1) was prepared similarly by the acylation of the diethylaminoethyl ester of D,L-phenylalanine with p-bis(2-chloroethyl)aminophenylacetic acid. The removal of the benzyl group from compounds of type (I) through catalytic hydrogenolysis in the presence of palladium black made it possible to obtain N-acylated amino-acids of type (II) (Table 2).

To prove the structure of (II), p-bis(2-chloroethyl)aminophenylacetic and γ -[p-bis(2-chloroethyl)aminophenyl]butyric acids were also prepared by the acylation of the corresponding amino-acids with the acid chlorides by the Schotten-Baumann reaction. The results of the biological tests will be described in a separate communication.

EXPERIMENTAL

Benzyl Esters of N-[p-bis(2-chloroethyl)aminophenylacetyl]- and N-(γ -[p-bis(2-chloroethyl)aminophenyl]butyryl)amino-acids (I)

General method of preparation. An equimolar mixture of bis(2-chloroethyl)amino-substituted phenylacetic or phenylbutyric acid, the benzyl ester of the amino-acid, and 1,3-dicyclohexylcarbodiimide in chloroform was allowed to stand overnight. The resulting precipitate of 1,3-dicyclohexylurea was filtered off, the chloroform evaporated in a vacuum, and the residue recrystallized. The analyses of the compounds obtained, the melting points, the yields and the salts used for recrystallization are given in Table 1.

N-[p-bis(2-chloroethyl)aminophenylacetyl]- and N-(γ -[p-bis(2-chloroethyl)aminophenyl]butyryl)amino-acids (II)

(a) Catalytic hydrogenolysis of the corresponding benzyl esters. A solution of the benzyl ester of N-[p-bis(2-chloroethyl)aminophenylacetyl]- or N-(γ -[p-bis(2-chloroethyl)aminophenyl]butyryl)-D,L-amino-acid in absolute methyl alcohol was shaken in the presence of 2% (with respect to the weight of the substance to be hydrogenated) of palladium black until absorption of hydrogen ceased. The catalyst was then filtered off, and two thirds of the solvent evaporated in a vacuum; the residue was treated with absolute ether and left to stand in the refrigerator until crystallization began. Analyses of the substances obtained, the melting points, the yields, and the solvents used for recrystallization are given in Table 2.

TABLE 1

No.	n	R'	R	Recrystallized from	M. p., °C	Yield, %	Found, %				Calculated, %			
							C	H	Cl	N	C	H	Cl	N
1	1	CH ₂ Ph	CH ₂ Ph	Ethyl acetate	122-123	90,0	65,64	6,07	13,95	—	65,48	5,89	13,89	—
2	1	CH(CH ₃) ₂	CH(CH ₃) ₂	Methanol	76-77	70,0	61,84	6,75	15,34	—	62,05	6,49	15,24	—
3	1	Ph	CH ₂ CH ₂ SCCH ₃	Ethanol	104-105	97,0	57,82	5,78	13,75	5,65	58,17	6,10	14,31	5,7
4	1	Ph	(CH ₂) ₂ COOCH ₂	Ethanol	78-79	60,0	63,07	5,80	12,00	—	63,58	5,85	12,12	—
5	1	Ph	(CH ₂) ₄ NH-CO	Ph	96-97	88,0	62,17	6,14	11,20	6,93	62,24	6,27	11,32	6,70
6	3	Ph	PhCH ₂ -O	Ph	87-88	70,0	66,24	6,27	13,04	—	66,53	6,35	13,10	—
7	1	(CH ₂) ₂ N(C ₂ H ₅) ₂	CH ₂ Ph	—	72-74	50,0	62,12	7,31	13,37	—	62,10	7,09	13,60	—

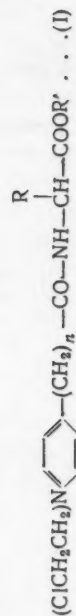
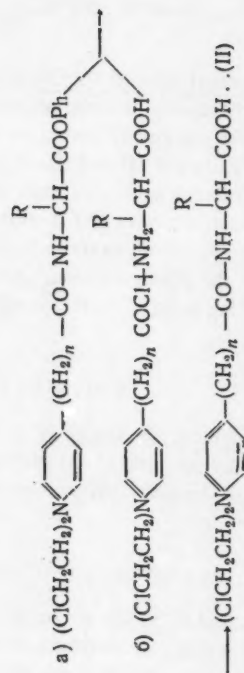


TABLE 2

No.	n	R	Recrystallized from	M. p., °C	Yield, %			Found, %				Calculated, %			
					a	b	c	C	H	Cl	N	C	H	Cl	N
1	1	CH ₂ Ph	Ethyl acetate + petroleum ether	125-126	83,0	65,00	59,62	5,70	16,45	6,73	59,71	5,45	16,82	6,63	—
2	1	CH(CH ₃) ₂	Benzene	120-121	87,5	73,0	53,40	6,15	17,41	—	54,39	6,44	18,90	—	—
3	1	(CH ₂) ₄ NH ₂	Methanol	159-160	66,0	—	52,84	6,78	17,00	10,44	53,46	6,73	17,54	10,39	—
4	1	CH ₂ CH ₂ SCCH ₃	Ethyl acetate + petroleum ether	122-123	—	50,0	49,95	6,03	—	—	50,15	5,90	17,44	6,88	—
5	3	CH ₂ Ph	Ether	99-101	82,0	45,0	60,99	6,21	15,17	7,03	61,19	6,25	15,7	—	—
6	3	CH(CH ₃) ₂	"	110-111	78,0	—	56,76	6,75	17,65	—	56,57	6,99	17,59	—	—
7	1	(CH ₂) ₂ COOH	Ethyl acetate + petroleum ether	100-103	83,0	57,0	50,67	5,74	17,02	6,82	50,38	5,41	17,49	6,91	—



(b) Acylation of the D,L-amino-acids with the acid chlorides of p-bis(2-chloroethyl)aminophenylacetic and γ -[p-bis(2-chloroethyl)aminophenyl]butyric acids. The acid chloride (0.001 mole) of p-bis(2-chloroethyl)aminophenylacetic or γ -[p-bis(2-chloroethyl)aminophenyl]butyric acid in 0.002 mole of NaOH was added with stirring to a solution of 0.001 mole of the D,L-amino-acid in 1 N NaOH (0.001 mole) cooled with ice water. To the mixture, which became thick, dioxan was added dropwise until the precipitate dissolved completely, and stirring was continued for a further 30 min. The solution was acidified with concentrated HCl to pH 3-4, the dioxan evaporated in a vacuum, and the aqueous residue extracted with chloroform. The extract was dried over magnesium sulfate, the solvent distilled off in a vacuum, and the dry residue washed with ether to remove traces of p-bis(2-chloroethyl)aminophenylacetic and γ -[p-bis(2-chloroethyl)aminophenyl]butyric acids, and recrystallized from an ethyl acetate - petroleum ether or benzene - petroleum ether mixture. The mixed melting point with the corresponding compound prepared by method "a" did not exhibit a depression. The yields of the substances obtained are given in Table 2.

Diethylaminoethyl Ester of p-bis(2-chloroethyl)aminophenylacetyl-D,L-phenylalanine

(a) Diethylaminoethyl ester of D,L-phenylalanine. A mixture of 3.3 g (0.02 mole) of D,L-phenylalanine and 4.8 g (0.4 mole) of diethylaminoethanol in 11.8 g (0.02 mole) of concentrated H_2SO_4 was heated on a water bath for 8 hr. The solution was then poured out onto ice, neutralized with Na_2CO_3 , and extracted with ether, the extract being then dried over magnesium sulfate. The residue, after the ether had been distilled off, was distilled in a vacuum. Yield 2.2 g (41.5%) of the diethylaminoethyl ester of D,L-phenylalanine; b. p. 120-122° (2 mm); n_D^{20} 1.5028; d 1.0196; found MR 76.90; calculated MR 76.51.

(b) Acylation of the diethylaminoethyl ester of D,L-phenylalanine. An equimolar mixture of p-bis(2-chloroethyl)aminophenylacetic acid (2.5 g), the diethylaminoethyl ester of D,L-phenylalanine obtained above (2.4 g), and 1,3-dicyclohexylcarbodiimide (1.8 g) was allowed to stand overnight in 10 ml of chloroform. The resulting precipitate of 1,3-dicyclohexylurea (1.5 g) was filtered off and the chloroform was removed in a vacuum. The oily residue was dissolved in 6 ml of ethyl acetate, treated with petroleum ether until the appearance of turbidity, and allowed to stand in the refrigerator. The additional quantity of 1,3-dicyclohexylurea was filtered off and the filtrate again treated with 15 ml of petroleum ether and allowed to stand in the refrigerator. The resulting crystalline precipitate was filtered off. Yield 2.4 g (50.0%) of the diethylaminoethyl ester of p-bis(2-chloroethyl)aminophenylacetyl-D,L-phenylalanine, m. p. 69-72°. The melting point after recrystallization from an ethyl acetate - petroleum ether mixture was 72-74°.

SUMMARY

N-[p-bis(2-chloroethyl)aminophenylacetyl]- and N-(γ -[p-bis(2-chloroethyl)aminophenyl]butyryl)-D,L-amino-acids were prepared by the catalytic hydrogenolysis of the corresponding benzyl esters or by acylation of the amino-acids with the acid chlorides of p-bis(2-chloroethyl)aminophenylacetic and γ -[p-bis(2-chloroethyl)aminophenyl]butyric acids.

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HYDROGEN ISOTOPE EXCHANGE IN ALKYL HALIDES

COMMUNICATION 4. HYDROGEN EXCHANGE BETWEEN TERT-ALKYL BROMIDES

AND ANHYDROUS ACETIC ACID IN THE PRESENCE OF APROTIC ACIDS

E. V. Bykova, V.N. Sekina, and D. N. Kursanov

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR

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Our previous investigations [1] showed that tert-alkyl bromides undergo hydrogen isotope exchange in acetic acid more readily than the chlorides, apparently because of the more pronounced ability of the carbon-bromine bond to ionize. This has found confirmation in the work of Ingold and co-workers [2], who showed that the rate of S_N1 solvolysis of tert-alkyl bromides is approximately 30 times greater than that of the corresponding tert-alkyl chlorides. The present work was undertaken to investigate the kinetics of hydrogen exchange in tert-alkyl bromides (tert-C₄H₉Br, 2-methyl-2-bromobutane, 2-methyl-2-bromopentane). Table 1 gives the rate constants for these reactions at 20, 30, and 40°.

TABLE 1. Hydrogen Exchange between tert-Alkyl Bromides and Acetic Acid

tert-R - Br	$k \cdot 10^{-4}, \text{sec}^{-1}$		
	20°	30°	40°
(CH ₃) ₃ CBr	0,6	3,7	14,1
(CH ₃) ₂ (C ₂ H ₅)CBr	1,5	—	—
(CH ₃) ₂ (C ₃ H ₇)CBr	1,9	11,0	46,0

TABLE 2. Rate of Hydrogen Exchange between tert-Alkyl Bromides and Acetic Acid in the Presence of Aprotic Acids

Halide	Catalyst		$k \cdot 10^{-6}, \text{sec}^{-1}$		
	formula	moles per mole of alkyl bromide	20°	30°	40°
tert-C ₄ H ₉ Br	HgBr ₂	0,05	6,1	11,7	53
	SnBr ₄	0,05	3,0	7,2	31,3
	GeBr ₄	0,05	0,06	—	—
	6/kat.	—	0,06	—	—
2-Methyl-2-bromopentane	HgBr ₂	0,03	—	28,0	—
	SnBr ₄	0,03	—	14,0	—
	HgBr ₂	0,05	27,2	103	274
	SnBr ₄	0,05	13,6	48,4	123

The data in Table 1 show that increase in the molecular weight of the tert-alkyl bromide leads to an increase in the hydrogen exchange. The same regularity was observed in the work of Ingold and co-workers [2] on the hydrolysis of tert-alkyl halides. This correspondence between S_N1 solvolysis and hydrogen exchange once again confirms that in acid media hydrogen atoms are exchanged in ionized molecules of the tert-alkyl halide.

We showed earlier that chlorides of metals having unsaturated coordination valencies (for example SnCl₄, HgCl₂, etc.) accelerate hydrogen exchange between tert-alkyl chlorides and acetic acid [3]. The mechanism of this effect

consists in the coordination of the halide anion to the metal, thereby completing its electron shell. This converts the alkyl residue to the carbonium ion, which is capable of hydrogen exchange [4].

TABLE 3. Relative Activity of HgBr_2 (k_1) and SnBr_4 (k_2) (molar ratio tert-AlkBr: CH_3COOH : $\text{MBr}_x = 1:10:0.5$)

tert-R - Br	k_1/k_2		
	20°	30°	40°
$(\text{CH}_3)_3\text{CBr}$	2,0	1,6	1,7
$(\text{CH}_3)_2\text{C}-\text{Br}$	2,0	2,1	2,2
C_8H_{17}	—	2,0*	—

* Molar ratio tert-Alk: CH_3COOH : $\text{MBr}_x = 1:10:0.3$.

It appeared of interest to investigate the effect of the bromides of these metals on the hydrogen exchange in tert-alkyl bromides. The bromides of boron and tin are much weaker complex-forming agents than their chlorides [5, 6]. We have investigated the rate of hydrogen exchange in tert-alkyl bromides (tert- $\text{C}_4\text{H}_9\text{Br}$ and 2-bromo-2-methylpentane) in the presence of HgBr_2 and SnBr_4 at 20, 30, and 40°, and GeBr_4 at 20° (Table 2).

Mercuric bromide and stannic bromide, like the chlorides, enhanced the rate of hydrogen exchange between tert-alkyl halides and acetic acid, whereas GeBr_4 did not.* It is interesting that mercuric-bromide proved to be twice as active as stannic bromide in the hydrogen exchange of tert-alkyl bromides (Table 3), whereas stannic chloride was 50 times as active as mercuric chloride in the hydrogen exchange involving tert-alkyl chlorides [3].

EXPERIMENTAL**

Deuteroacetic acid, prepared by the decomposition of acetic anhydride with deuterium oxide, had an excess density of 11,000–15,000 $\mu\text{g/ml}$. The acid employed in the experiments contained 0.1–0.4% of the anhydride. The following aprotic acids were employed: commercial HgBr_2 purified by threefold sublimation [7]; SnBr_4 and GeBr_4 , prepared as described in [8, 9] and purified by distillation at atmospheric pressure. tert-Butyl bromide, 2-methyl-2-bromobutane, and 2-methyl-2-bromopentane were prepared by treating the corresponding alcohols with hydrobromic acid or gaseous HBr .

Physical Constants of the Initial tert-Alkyl Bromides

tert-Alkyl bromide	B.p., °C (p, mm Hg)	n_D^{20}	d_4^{20}
$\text{C}_4\text{H}_9\text{Br}$	73,0–73,2	1,4280	1,2230
2-Methyl-2-bromobutane	54–55(126)	1,4420	1,1932
2-Methyl-2-bromopentane	59(60)	1,4450	1,1571

Since all the experiments on hydrogen exchange in tert-alkyl bromide were carried out in the way already described [10], only a few are quoted.

tert-Butyl bromide in acetic acid in the presence of SnBr_4 . SnBr_4 [1.32 g (3 millimoles)] was dissolved in 36.73 g (612 millimoles) of acetic acid (excess density 14,000 $\mu\text{g/ml}$), treated with 8.24 g (60 millimoles) of tert-butyl bromide, and placed in a thermostat at 20°.

Sampling time, hr	EDCW* of the bromide, $\mu\text{g/ml}$	$k \cdot 10^6, \text{sec}^{-1}$	Average k, sec^{-1}
20	1470	3,06	$3,0 \cdot 10^{-6}$
23	1620	2,94	
24	1710	3,00	

* Excess density of combustion water (water formed on combustion).

* GeCl_4 also does not accelerate the hydrogen exchange between 2-methyl-2-chloropentane and acetic acid. At 40° the rate constant for the hydrogen exchange in the presence of GeCl_4 proved to be $2.3 \cdot 10^{-7} \text{sec}^{-1}$, and in its absence $2.2 \cdot 10^{-7} \text{sec}^{-1}$.

** Laboratory technician A. I. Golovanova participated in the experimental work.

tert-Butyl bromide in acetic acid without catalyst. *tert*-Butyl bromide [5.90 g (43 millimoles)] was dissolved in 25.54 g (426 millimoles) of acetic acid (excess density 14,230 $\mu\text{g/ml}$) and the solution allowed to stand at room temperature.

Sampling time, hr	EDCW of the bromide, $\mu\text{g/ml}$	$k \cdot 10^8$, sec^{-1}	Average k , sec^{-1}
216	336	5,6	$6 \cdot 10^{-8}$
288	450	5,9	
456	678	5,6	

tert-Butyl bromide in acetic acid in the presence of GeBr_4 . GeBr_4 [0.49 g (1.2 millimoles)] was dissolved in 15.24 g (250 millimoles) of acetic acid (excess density 14,860 $\mu\text{g/ml}$); the solution was treated with 3.70 g (27 millimoles) of *tert*-butyl bromide and allowed to stand at room temperature.

Sampling time, hr	EDCW of brom- ide, $\mu\text{g/ml}$	$k \cdot 10^8$, sec^{-1}	Average k , sec^{-1}
235	450	5,2	$6 \cdot 10^{-8}$
332	595	6,9	
407	678	6,4	

2-Methyl-2-bromopentane in acetic acid in the presence of HgBr_2 . HgBr_2 [0.78 g (2.2 millimoles)] was dissolved in 26.24 g (437 millimoles) of acetic acid (excess density 14,860 $\mu\text{g/ml}$); the solution was treated with 7.15 g (43.4 millimoles) of 2-methyl-2-bromopentane and placed in a thermostat at 20°.

Sampling time, hr	EDCW of the bromide, $\mu\text{g/ml}$	$k \cdot 10^5$, sec^{-1}	Average k , sec^{-1}
2	930	2,77	$2,72 \cdot 10^{-5}$
2,5	1070	2,74	
3,0	1280	2,68	

2-Methyl-2-bromopentane in acetic acid in the presence of SnBr_4 . SnBr_4 [1.07 g (2.45 millimoles)] was dissolved in 29.44 g (490 millimoles) of acetic acid (excess density 14,860 $\mu\text{g/ml}$); the solution was treated with 8.25 g (50 millimoles) of 2-methyl-2-bromopentane and placed in a thermostat at 20°.

Sampling time, hr	EDCW of the bromide, $\mu\text{g/ml}$	$k \cdot 10^5$, sec^{-1}	Average k , sec^{-1}
240	900	1,38	$1,36 \cdot 10^{-5}$
280	1050	1,39	
320	1100	1,30	
360	1282	1,35	

SUMMARY

1. A study has been made of the hydrogen exchange between *tert*-alkyl bromides and acetic acid (*tert*-butyl bromide, 2-methyl-2-bromobutane, 2-methyl-2-bromopentane). The same regularities have been observed in the hydrogen exchange as in the $\text{S}_{\text{N}}1$ solvolysis, which confirms that the hydrogen exchange takes place via the carbonium ion.

2. The rate of hydrogen exchange of *tert*-butyl bromide and 2-methyl-2-bromopentane with acetic acid in the presence of HgBr_2 and SnBr_4 has been studied at 20, 30, and 40°. The rate of the reaction catalyzed by HgBr_2 is twice as high as that catalyzed by SnBr_4 .

3. A study has been made of the hydrogen exchange between tert-butyl bromide and acetic acid in the presence of GeBr_4 and between 2-methyl-2-chloropentane and acetic acid in the presence of GeCl_4 . It has been shown that GeBr_4 and GeCl_4 do not accelerate the hydrogen exchange under these conditions, i.e., they do not exhibit their coordination-valency unsaturation.

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REFORMING OF GASOLINE FRACTIONS OF VOLGA-URAL CRUDES ON RHENIUM-ALUMINA CATALYST TREATED WITH HYDROGEN SULFIDE

Kh. M. Minachev, M. A. Ryashentseva, and V. A. Petrukhov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

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In a previous communication [1] we presented experimental data obtained on reforming automotive gasoline (separated from Volga-Ural crudes) on a rhenium-alumina catalyst. This catalyst contained 20% rhenium on aluminum oxide, and received supplementary treatment with hydrogen sulfide. The catalyzate obtained as a result of reforming the original gasoline contained 32-47% aromatic hydrocarbons and had an octane number of 87.2. After 108 hr of operation the catalyst had fallen off considerably in activity and was subjected to regeneration. It was demonstrated that the catalyst was thereby restored almost completely to its initial activity. For examining the possibility of repeated regeneration of the 20% Re - Al_2O_3 catalyst treated with hydrogen sulfide, a more detailed study was undertaken on the process of reforming the gasoline fraction of Volga-Ural crude at 500-510°, $v = 1.0 \text{ hr}^{-1}$, $\text{H}_2 : \text{HC} = 5 : 1$, and pressure 5 atm. The catalyst under investigation operated about 500 hr (including regenerations) and showed high aromatizing and desulfurizing capability.

EXPERIMENTAL

A 20% rhenium-alumina catalyst treated with hydrogen sulfide was prepared by a method we described previously [2]. For reforming the gasoline fraction, the reactor was charged with 30 ml of catalyst. The experiments were conducted in a flow-type unit [3] at 500-510°, 5 atm hydrogen pressure, feedstock space velocity 1.0 hr^{-1} , and molar ratio of H_2 to gasoline $\text{H}_2 : \text{HC} = 5 : 1$. The resulting catalyzates were characterized by specific gravity, refractive index, and sulfur content. The quantity of aromatic hydrocarbons in the catalyzates was determined on the basis of ultraviolet absorption spectra taken in a vacuum spectrophotometer, converted from an SP-41 monochromator. The following elements of the spectrophotometer were constructed: Strong source of continuous light (hydrogen lamp with fluorite window), cuvette portion filled with nitrogen, and fluorite cuvettes. All of this made it possible to obtain absorption spectra down to 1700 Å, while the existing SF-4 apparatus operates reliably only down to 2300 Å. The use of the vacuum spectrophotometer gives fuller information, permitting both qualitative and quantitative analysis of the mixture. Several absorption bands whose maxima do not overlap fall within the working range of the apparatus. Thus, for example, the absorption maximum in the main transition for benzene lies in the 1840 Å region, and for toluene in the 1880 Å region. This permits qualitative analysis of the mixture. In addition, the spectrum of aromatic hydrocarbons has a characteristic second wide band in the range 1950-2000 Å, with an approximately constant molar absorption coefficient $\epsilon = 8000$. A quantitative estimation can be made on the basis of this band, since the percentage content of aromatic hydrocarbons is proportional to the absorption in this transition. The absorption spectra of gasoline mixtures with differing content of aromatic hydrocarbons are shown in Fig. 1. The error obtained in the vacuum monochromator constitutes not more than $\pm 5\%$.

The properties of the initial gasoline fraction and the catalyzates obtained by reforming under the conditions indicated above are presented in the table and in Fig. 2. As is evident from these data, a considerable enrichment of the gasoline fraction with aromatic hydrocarbons takes place in the process of reforming on Re - Al_2O_3 catalyst treated with hydrogen sulfide. Thus, after the first 22 hr of catalyst operation the aromatic hydrocarbon content is increased from 6.6 to 68%, which constitutes an increase of 61.4%, the aromatic hydrocarbons being formed not only on account of dehydrogenation and dehydroisomerization of naphthenic hydrocarbons, but also on account of dehydrocyclization of paraffinic hydrocarbons (see table). The occurrence of these reaction on rhenium-alumina catalyst treated with hydrogen sulfide had been demonstrated by us previously [2]. In addition to the reactions of dehydrogenation, dehydroisomerization, and dehydrocyclization, this catalyst also leads to desulfurization. Thus, the content of sulfur compounds in the catalyzates is reduced from 0.017 to 0.001-0.007%. The content of aromatic

Characteristics of Initial Gasoline Fraction and Catalyzates Obtained by Reforming
(500-510°, 5 atm, $v = 1.0 \text{ hr}^{-1}$, and $\text{H}_2 : \text{HC} = 5:1$)

Properties	Initial gasoline fraction	Properties of catalyzates					
		after 22-hr catalyst operation	after 1st regeneration (112 hr)	after 2nd regeneration (190 hr)	after 3rd regeneration (70 hr)	after 4th regeneration (55 hr)	after 5th regeneration (39 hr)
Refractive index, n_D^{20}	1,4045	1,4500	1,4600	1,4375	1,4300	1,4220	1,4200
Specific gravity, d_4^{20}	0,7197	0,7820	0,7950	0,7640	0,7535	0,7445	0,7400
Content of aromatic hydrocarbon, wt. %	6,6	68,0	77,0	48,0	39,0	28,5	26,0
Content of sulfur compounds, wt. %	0,017	0,002	0,007	0,006	0,006	0,005	0,007
Engler distillation, °C							
IBP	89,5	46,0	54,0	51,0	55,0	67,0	72,0
10%	93,0	79,5	82,0	79,0	80,5	86,0	84,5
50%	99,5	96,0	96,0	96,0	95,0	96,5	96,0
90%	113,0	114,5	113,0	116,0	111,0	110,5	113,5
97,5%	126,0	132,0	133,0	133,0	134,0	132,0	128,0
FBP	126,0	135,0	138,5	133,0	145,0	138,0	138,5

Note: Group composition (wt. %) [4]: Paraffinic hydrocarbons 52.7%, naphthenic 33.1% (including 14.6% five-membered and 18.5% six-membered), and aromatic 6.6%.

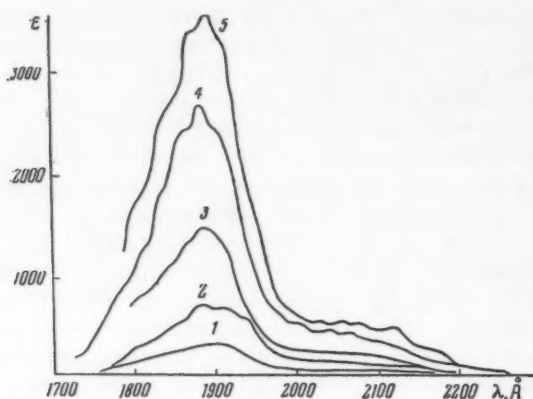


Fig. 1. Absorption spectra of gasoline mixtures with differing content of aromatic hydrocarbons: 1) 5.5%; 2) 13.0%; 3) 26%; 4) 56.0%; 5) 68.07%.

hydrocarbons, as is evident from Fig. 2, gradually decreases in proportion to the gasoline fraction throughout. After 35 hr of catalyst operation it was reduced to 20% and remained at this level during the succeeding 60 hr. After this, as the content of aromatic hydrocarbons in the catalyzate was reduced to 12%, the catalyst was regenerated. The first cycle of catalyst operation constituted 112 hr, after which regeneration was carried out. This was performed in a stream of nitrogen with the addition of 2.5-3% oxygen with a stepwise increase of temperature to 400°. On reaching this temperature the regeneration was continued for 5-6 hr, after which the catalyst was treated with hydrogen at 400° for 5 hr.

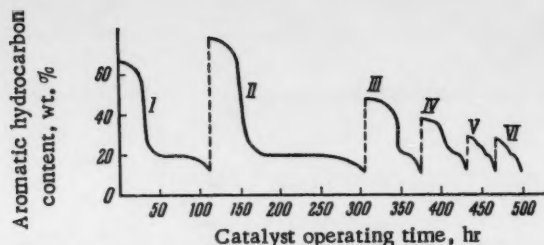


Fig. 2. Aromatic hydrocarbon content (wt. %) as a function of catalyst operating time (hr): I-VI Cycles of operation of catalyst.

As is evident from the data of the table and Fig. 2, the catalyst after the first regeneration recovered its original properties, the content of aromatic hydrocarbons in the catalyzate even being somewhat increased. During the first 30 hr of catalyst operation the content of aromatic hydrocarbons in the catalyzate constituted on the average about 68%. Later the catalyst activity gradually decreased, and the content of aromatic hydrocarbons after 60 hr operation constituted 20%. The catalyst retained this activity for 56 hr of operation. In 190 hr the content of aromatic hydrocarbons in the catalyzate was reduced to 12%, and the catalyst was subjected to a secondary regeneration. After the second regeneration it also had a high aromatizing capability. Thus, the content of aromatic hydrocarbons in the catalyzate constituted 49%; however, the catalyst stability was already less than after the first regeneration by a factor of 2.7. The third catalyst regeneration was conducted after 70 hr of operation. A total of five catalyst regenerations were performed, and it was found that although each regeneration restores the aromatizing capability of the catalyst to a considerable degree, its stability is decreased markedly. The content of sulfur compounds in the catalyzate during 500 hr of catalyst operation with regenerations is decreased by an average factor of almost 3. It should be indicated that in the first 2-3 hr of operation and also after the first two regenerations the catalyst has significant hydrocracking properties (about 40-50%). However, the hydrocracking capability of the catalyst drops rapidly, and after 3-4 hr of operation the gas formation is only 4-5%.

SUMMARY

1. An investigation has been made of the catalytic properties of 20% rhenium-alumina catalyst treated with hydrogen sulfide in reforming an 89.5-126° gasoline fraction of Volga-Ural [petroleum] deposit at 500-510°, 5 atm hydrogen pressure, $v = 1.0 \text{ hr}^{-1}$, and $\text{H}_2 : \text{HC} = 5 : 1$ during a 500 hr period, including regeneration.
2. Under the chosen conditions the content of aromatic hydrocarbons was successfully increased from 6 to 20-60%, and the content of sulfur compounds was lowered from 0.017 to 0.002-0.007%.
3. An approximate method has been proposed for total determination of aromatic hydrocarbon content in catalyzates by an optical method using a vacuum monochromator.

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DETERMINATION OF INDIVIDUAL HYDROCARBON COMPOSITION
OF TATAR CRUDES

COMMUNICATION 5. LIGROIN FROM CRUDE OF THE BAVLY DEPOSIT

B. Le, R. I. Izmailov, F. A. Urmancheev, I. P. Lipatova,
S.-Kh. G. Kashaev, I. A. Lamanova, and R. G. Bukharaeva
A. E. Arbuzov Chemical Institute, Academy of Sciences of the USSR (Kazan' Branch)
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
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In an investigation of the individual hydrocarbon composition of the gasolines (b. p. to 150°) from Devonian crudes of the Romashkino and Bavly deposits it was shown that the gasolines from these deposits differ in the basic distribution of normal- and iso-structure paraffins [1]. Therefore, it was of interest to study the individual and group hydrocarbon composition of the ligroins from crudes of these deposits. Previously [2] data were set forth from an investigation of the hydrocarbon composition of the ligroin fraction of crude from the Romashkino deposit. In all there were detected 39 hydrocarbons of differing structure, and their quantitative content in the ligroin was given. In the present work results are presented from an investigation of the ligroin (150-200°) of crude from the Bavly deposit.

EXPERIMENTAL

The procedure and methods of analysis of the ligroin were set forth in a previous communication [2]. The ligroin was obtained from a wide fraction, 120-240°, in a column with 40 theoretical plates. A 146-205° fraction was taken, having d_4^{20} 0.7745, n_D^{20} 1.4332. By chromatography of the segregated ligroin there were obtained: 1) naphthenoparaffins 83.1% (d_4^{20} 0.7581, n_D^{20} 1.4216), 2) aromatics "A" 14.4% (d_4^{20} 0.8740, n_D^{20} 1.5001), 3) yellow portion 1.8% (mixture of aromatic and sulfur-containing hydrocarbons, S = 1.03%), and 4) losses, 0.7%.

By analytical dehydrogenation of the naphtheno-paraffins on iron-platinized carbon [3], a catalyzate (d_4^{20} 0.7668, n_D^{20} 1.4294) was obtained with 90.6% yield, which consisted 88.8% of naphtheno-paraffins "NP" and 9.7% of aromatic hydrocarbons "A_N" (dehydrogenated naphthenes). The aromatic (A and A_N) and the naphtheno-paraffinic (NP) hydrocarbons were distilled in a column with 40 theoretical plates into narrow fractions, whose physicochemical constants were determined. The calculation of the aromatic and naphthenic rings in the narrow aromatic fractions was based on specific dispersion [4], and the individual hydrocarbon composition on Raman spectra. The group composition of the naphtheno-paraffinic hydrocarbons NP was calculated according to the specific refraction of the narrow fractions.

Determination of composition of aromatic hydrocarbons. A 100-ml (83.8-g) sample of fraction A was taken for distillation. The yields of the narrow fractions, their physical constants, and their contents of naphthenic and aromatic rings are shown in Table 1.

From Table 1 it is evident that fractions I, II, III, V, VI, IX, and XI did not contain naphthenic rings, but aromatic hydrocarbons with naphthenic rings were present in fractions IV, VII, VIII, X, and XII. Of these fractions, VII had the greatest quantity of naphthenic rings. According to the boiling point of this fraction, a content of indan is probable (b. p. 177.9 [5]); indeed, indan was detected in this fraction by spectral analysis. Fraction X (b. p. 185.5-191°) contained naphthenic rings, but the structure of these naphtheno-aromatic hydrocarbons was not determined successfully by the spectral method.

The individual aromatic hydrocarbons in the ligroin, determined by the Raman spectrum method, are shown in Table 2.

TABLE 1

Fraction	Dist. range, °C	Content in ligroin, %	d_4^{20}	n_D^{20}	R_a	R_H
I	149 —155	0,38	0,8567	1,4915	0,98	—
II	155 —163	1,74	0,8620	1,4960	0,98	—
III	163 —167	2,55	0,8689	1,5000	0,99	—
IV	167 —171	1,44	0,8739	1,5030	1,00	0,05
V	171 —174	0,55	0,8778	1,5035	1,01	—
VI	174 —176,5	0,92	0,8752	1,5037	1,00	—
VII	176,5—179	0,45	0,8727	1,5008	0,99	0,17
VIII	179 —182,5	0,61	0,8686	1,4989	0,97	0,06
IX	182,5—185,5	0,82	0,8683	1,4989	1,01	—
X	185,5—191	1,28	0,8745	1,5011	0,99	0,12
XI	191 —195	0,66	0,8786	1,5040	1,09	—
XII	195 —200	0,71	0,8855	1,5078	1,08	0,1
	Residue	1,31				
	Losses	0,98				
Total		14,4				

TABLE 2

Fraction	Hydrocarbon	Contents in ligroin, %	Fraction	Hydrocarbon	Contents in ligroin, %
I	Isopropylbenzene	0,38*	XV	1,2-Dimethyl-3-ethylbenzene	0,10
II	n-Propylbenzene	0,48	XVI	1,2-Dimethyl-4-ethylbenzene	0,42
III	1-Methyl-2-ethylbenzene	0,42	XVII	1,3-Dimethyl-2-ethylbenzene	0,04
IV	1-Methyl-3-ethylbenzene	0,87	XVIII	1,3-Dimethyl-5-ethylbenzene	0,34
V	1-Methyl-4-ethylbenzene	0,73	XIX	1,4-Dimethyl-2-ethylbenzene	0,13
VI	1,2,3-Trimethylbenzene	0,95	XX	1,2-Diethylbenzene	0,18
VII	1,2,4-Trimethylbenzene	2,89	XXI	1,2,3,4-Tetramethylbenzene	0,18
VIII	1,3,5-Trimethylbenzene	1,01	XXII	1,2,3,5-Tetramethylbenzene	0,78
IX	sec-Butylbenzene	0,06	XXIII	1,3-Diisopropylbenzene	+
X	n-Butylbenzene	0,36	XXIV	Indan	+
XI	1-Methyl-3-isopropylbenzene	0,05	XXV	1,2-Diisopropylbenzene	10,54
XII	1-Methyl-3-n-propylbenzene	0,06		Identified	1,57
XIII	1-Methyl-4-isopropylbenzene	0,10		Not identified	
XIV	1-Methyl-4-n-isopropylbenzene	0,07			

* According to distillation.

As is evident from Table 2, mainly aromatic hydrocarbons C_9 and C_{10} have been identified. Among the C_9 aromatics, those present in the greatest quantity are the trimethylbenzenes* (1,2,4-trimethylbenzene > 1,3,5-trimethylbenzene > 1,2,3-trimethylbenzene), in almost 2,5 times the quantity of the methylethylbenzenes.

The determination of the composition of the aromatics A_n was carried out the same as for the aromatics A. The properties of the narrow fractions are shown in Table 3.

* A considerable quantity of 1,2,4-trimethylbenzene and its analogs was detected in the 150-250° fraction of Emba crude [6].

TABLE 3

Fraction	Dist. range, °C	Content in ligroin, %	d_4^{20}	n_D^{20}	R_a	R_H
I	150—160	0,68	0,8488	1,4854	1,07	—
II	160—171	0,68	0,8588	1,4920	0,95	—
III	171—175	0,17	0,8658	1,4939	0,95	0,02
IV	175—179	0,38	0,8666	1,4950	0,94	0,10
V	179—182,5	0,75	0,8665	1,4951	0,96	0,05
VI	182,5—185,5	0,56	0,8668	1,4952	0,96	0,06
VII	185,5—190	0,31	0,8721	1,4973	0,96	0,12
VIII	190—196	0,40	0,8729	1,4988	0,97	0,13
IX	196—205	0,84	0,8767	1,5000	0,97	0,17
	Residue	2,10				
	Losses	0,63				
	Initial fraction	7,5	0,8742	1,5100		

* Calculated as hydroaromatic hydrocarbons.

TABLE 4

Fraction	Aromatic hydrocarbon	Corresponding naphthene	Content in ligroin, %
I	Isopropylbenzene	Isopropylcyclohexane	0,17
II	Propylbenzene	Propylcyclohexane	0,60
II	1-Methyl-2-ethylbenzene	1-Methyl-2-ethylcyclohexane	0,04
IV	1-Methyl-3-ethylbenzene	1-Methyl-3-ethylcyclohexane	0,26
V	1-Methyl-4-ethylbenzene	1-Methyl-4-ethylcyclohexane	0,18
VI	1,2,3-Trimethylbenzene	1,2,3-Trimethylcyclohexane	0,19
VII	1,2,4-Trimethylbenzene	1,2,4-Trimethylcyclohexane	0,14
VIII	1,3,5-Trimethylbenzene	1,3,5-Trimethylcyclohexane	traces
IX	Isobutylbenzene	Isobutylcyclohexane	0,05
X	sec-Butylbenzene	sec-Butylcyclohexane	0,11
XI	Butylbenzene	Butylcyclohexane	0,47
XII	1-Methyl-3-isopropylbenzene	1-Methyl-3-isopropylcyclohexane	traces
XIII	1-Methyl-3-propylbenzene	1-Methyl-3-propylcyclohexane	0,25
XIV	1-Methyl-4-isopropylbenzene	1-Methyl-4-isopropylcyclohexane	0,06
XV	1-Methyl-4-propylbenzene	1-Methyl-4-propylcyclohexane	0,14
XVI	1,2-Diethylbenzene	1,2-Diethylcyclohexane	0,04
XVII	1,2-Dimethyl-3-ethylbenzene	1,2-Dimethyl-3-ethylcyclohexane	0,04
XVIII	1,2-Dimethyl-4-ethylbenzene	1,2-Dimethyl-4-ethylcyclohexane	0,11
XIX	1,2-Dimethyl-5-ethylbenzene	1,2-Dimethyl-5-ethylcyclohexane	0,03
XX	1,3-Dimethyl-2-ethylbenzene	1,3-Dimethyl-2-ethylcyclohexane	0,04
XXI	1,4-Dimethyl-2-ethylbenzene	1,4-Dimethyl-2-ethylcyclohexane	traces
XXII	1,2,3,4-Tetramethylbenzene	1,2,3,4-Tetramethylcyclohexane	0,08
XXIII	1,2,3,5-Tetramethylbenzene	1,2,3,5-Tetramethylcyclohexane	0,05
XXIV	1,2-Diisopropylbenzene	1,2-Diisopropylcyclohexane	0,09
XXV	1,3-Diisopropylbenzene	1,3-Diisopropylcyclohexane	0,04
XXVI	Idan	Hydrindan	0,02
		Identified	3,20
		Not identified	1,57

The data of Table 3 demonstrate that there are no naphthenic rings in the first two fractions, but in fractions IV, VII, VIII, and IX the content of naphthenic rings is above 10%. Indan (0,02% based on ligroin) was detected in fraction IV by the spectral method. Homologs of indan are possibly present in the higher boiling fractions.

TABLE 5

Fraction	Dist. range, °C	Content in ligroin, %	d_4^{20}	n_D^{20}	Content of hydrocarbons, %	
					naphthenes	paraffins
I	146—149	5,44	0,7277	1,4083	0,87	4,57
II	149—153	1,99	0,7335	1,4128	0,28	1,71
III	153—157	0,99	0,7495	1,4190	0,25	0,74
IV	157—162,5	2,32	0,7504	1,4199	0,81	1,51
V	162,5—166	4,18	0,7551	1,4220	1,30	2,88
VI	166—170	2,78	0,7519	1,4210	0,78	2,00
VII	170—172	1,79	0,7472	1,4198	0,27	1,52
VIII	172—175	8,61	0,7437	1,4179	1,46	7,15
IX	175—179	2,06	0,7525	1,4219	0,31	1,75
X	179—184	4,12	0,7629	1,4261	1,56	2,56
XI	184—190	3,32	0,7694	1,4290	1,62	1,70
XII	190—194	5,32	0,7624	1,4258	0,88	4,44
XIII	194—197	6,03	0,7538	1,4233	0,36	5,67
XIV	197—200	1,52	0,7664	1,4277	0,43	1,09
	Residue	11,92				
	Losses	3,91				
Total		66,30			11,18	39,29

TABLE 6

Fraction	Groups of hydrocarbons	Number of hydro- carbons	Content ligroin, %
I	Normal hydrocarbons C_9-C_{11}	3	19,1
II	Branched paraffinic hydrocarbons $C_{10}-C_{12}$	—	20,19
III	Pentamethylene hydrocarbons $C_{10}-C_{12}$	—	11,18
IV	Hydroaromatic hydrocarbons C_9-C_{12}	25	3,18
V	Derivatives of benzene C_9-C_{10}	22	10,5
VI	Hydrindan	1	0,02
VII	Indan and its derivatives	1	traces
Total		52	64,17

The hydrocarbons found by the spectral method are presented in Table 4. The aromatics A_n were identified to the extent of 72,8%.

From Table 4 it is evident that among the hydroaromatic hydrocarbons those present in the greatest quantity are propylcyclohexane and butylcyclohexane, i.e., cyclohexanes having an alkyl radical of normal structure. On comparing the data of Tables 2 and 4 it is evident that the content of propylcyclohexane and butylcyclohexane in the ligroin is greater than that of propylbenzene and butylbenzene respectively, even though the total quantity of hydroaromatics is less than that of aromatic hydrocarbons. The isomers of methylpropylbenzenes are distributed among themselves approximately equally (Table 2, fractions XI, XII, XIII, and XIV), but for the corresponding hydroaromatic hydrocarbons, isomers of normal structure predominated (1-methyl-3-propylcyclohexane > 1-methyl-3-isopropylcyclohexane; 1-methyl-4-propylcyclohexane > 1-methyl-4-isopropylcyclohexane; Table 4, fractions XIII, XII, XV, and XIV).

Determination of structural-group composition of naphtheno-paraffins "NP". Distillation of the naphtheno-paraffinic portion in a column with 40 theoretical plates gave 14 fractions. A 200-ml (152,3-g) quantity of the naphtheno-paraffins was taken for distillation. The physicochemical properties of the narrow fractions which were segregated are shown in Table 5.

From Table 5 is evident that the naphthenes are less than the paraffins by a factor of 3.5. Fraction VIII contained a considerable quantity of the [total] paraffins and, according to the boiling point, corresponded to n-decane. Fraction XIII evidently is represented mainly by n-undecane.

In the investigation of the gasolines distilling to 150°, it had been shown that the isoparaffins have predominantly a slightly branched structure. Therefore, it may be assumed that the ligroin fractions likewise include very little of highly branched paraffins. Proceeding from this basis, the C₁₀ paraffinic hydrocarbons should distill between 153 and 174°, and the C₁₁ between 174 and 197° [7]; thus the fractions III-VIII contain 8.65% isodecanes and 7.15% n-decane, and the fractions IX-XIII contain 14.5% isoundecanes and 5.67% n-undecane. The total quantity of paraffinic hydrocarbons C₁₀ and C₁₁ is the same (15.8 and 16.12% respectively). The distribution of the group composition of the ligroin is shown in Table 6.

As a result of the investigation, 52 hydrocarbons have been detected, including 22 derivatives of benzene, 25 hydroaromatic hydrocarbons, 3 normal paraffins, and indan and hydrindan. From Table 6 it is evident that the contents of normal- and iso-structure paraffins in the ligroin are approximately equal; the hydroaromatic quantity is less than the aromatic hydrocarbon quantity by a factor of 3.

SUMMARY

1. The individual and group hydrocarbon composition of the 150-200° ligroin of Bavl crude has been investigated; thereby 23 aromatic and 26 hydroaromatic hydrocarbons have been detected, and their contents have been determined by a Raman spectrum method.

2. The total quantity of pentamethylene and paraffinic hydrocarbons has been calculated on the basis of specific refraction of the narrow fractions.

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CONVERSIONS OF CYCLOHEXANE ON PALLADINIZED GUMBRINE UNDER HYDROGEN PRESSURE

N. I. Shuikin, Kh. M. Minachev, M. A. Ryashentseva,
and Yu. A. Afanas'eva

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR
Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk*,
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In our previous investigations [1-6] a study was made of the catalytic properties of palladium, deposited in a quantity of 0.5-1% on aluminum oxide and silica gel, in the conversions of n-hexane, n-pentane, methylcyclopentane, ethylcyclopentane, cyclohexane, methylcyclohexane, and ethylcyclohexane. On catalysis in a flow-type unit at 460° and 20 atm hydrogen pressure these hydrocarbons undergo various deep conversions. Thereby the six-membered cyclanes are subjected mainly to dehydrogenation to the corresponding aromatic hydrocarbons and partially to isomerization with contraction of the ring to a five-membered. Recently one of us studied the catalytic properties of palladinized gumbrine catalysts in the case of conversions of the higher alkanes [7, 8]. In these investigations their isomerizing, hydrocracking, and dehydrocyclizing ability were demonstrated.

In the present work we decided to extend this investigation to the region of six-membered cyclanes. Results are cited below, obtained in studying the catalytic conversions of cyclohexane in the presence of palladinized gumbrine catalysts differing among themselves in method of pretreatment, under conditions of high pressures and temperature in a flow system.

It was found that a 0.5% palladinized gumbrine catalyst at 470°, 20 atm hydrogen pressure, space velocity $v = 1.0 \text{ hr}^{-1}$, and molar ratio of hydrogen to hydrocarbon $\text{H}_2 : \text{HC} = 5 : 1$ has not only dehydrogenating, but also a pronounced isomerizing action; thereby the contents of benzene and methylcyclopentane in the catalyzate are respectively 28.5 and 19.2%. It should be pointed out that the carrier alone (activated gumbrine) under the conditions indicated above leads to the reaction of cyclohexane isomerization, since the catalyzate, in addition to unchanged cyclohexane, contains 19.2% methylcyclopentane. Supplementary treatment of the catalyst with hydrogen sulfide leads to an increase of its dehydrogenating and isomerizing activity. Thus, the catalyzate contains 40.2% benzene and 22.7% methylcyclopentane. For establishing the palladium content in palladinized gumbrine catalysts, we developed a colorimetric method of determination.

EXPERIMENTAL

Activated gumbrine from the Georgian SSR [8] of composition SiO_2 86.98%, Al_2O_3 4.14%, Fe_2O_3 0.56%, MgO 1.27%, CaO 1.33%, TiO_2 0.41% and specific surface $260 \text{ m}^2/\text{g}$ was pressed into $4 \times 4 \text{ mm}$ tablets and calcined in a muffle furnace at 500° for 4-5 hr. Catalyst 1 was prepared by impregnating the gumbrine with a palladous chloride solution at room temperature, drying at 120° in a drying cabinet, and reducing with electrolytic hydrogen at 400° for 10 hr. Catalyst 2 differed from catalyst 1 in that it (2) was additionally treated with hydrogen sulfide at 120° for 4 hr in a flow system. The flow apparatus for operation under pressure and the method of analysis of the catalyzates was described in detail in our previous studies [3, 9]. The experiments with cyclohexane were conducted at 475-480°, hydrogen pressure 20 atm, $v = 1.0 \text{ hr}^{-1}$, and $\text{H}_2 : \text{HC} = 5 : 1$. First the cyclohexane was passed through the catalyst bed for 1 hr (preexperiment period), after which the experiment was carried out for 3-5 hr. The apparent volume of the catalyst was 5 ml. The cyclohexane taken for investigation was chemically pure and was characterized by n_D^{20} 1.4262 and d_4^{20} 0.7781. The catalyzates from the cyclohexane were analyzed by means of gas-liquid chromatography.

For control of the palladium content on the carrier in preparing the palladinized gumbrine catalysts, we developed a colorimetric method of palladium determination. Recently a method was proposed by Shmulyakovskii [10]

for determining platinum in platinized alumina catalysts; however, there are no studies dealing with the determination of palladium in catalysts of similar nature. Our proposed method is based on the color reaction of palladium with stannous chloride in hydrochloric acid medium [11], with preliminary extraction of the metal from the palladinized gumbrine catalysts by a mixture of concentrated HCl and H₂O₂ [12].

The present method was checked out on freshly prepared and on spent palladinized gumbrine catalysts. The palladium content in the catalyst was determined by means of an FEK-M photocolormeter by comparing the magnitude of optical density of a solution of palladium complex with stannous chloride with a standard curve expressing the magnitude of optical density of solutions of the palladium complex as a function of palladium concentration. For plotting the curve, we prepared standard solutions of the palladium complex with stannous chloride, containing palladium in quantities of 0.0012, 0.0036, and 0.006 mg/ml and on up to 0.024 mg/ml at intervals of 0.0024 mg/ml. The standard solutions were prepared in the following manner. A 0.5000-g sample of chemically pure palladous chloride was placed in a glass beaker and treated with a mixture of concentrated HCl with 5 ml H₂O₂ (sp. gr. 1.10) with heating on a steam bath for 15 min. The resulting solution was transferred to a 50-ml volumetric flask, made up to the mark with distilled water, and mixed; it contained 6 mg palladium per ml. Standard solutions of the indicated concentrations were prepared in 50-ml volumetric flasks, introducing a determined quantity of the palladous chloride solution and 1 ml of 10% stannous chloride solution in concentrated HCl; the contents were diluted with distilled water to the mark and mixed. The optical density of the prepared standard solutions relative to distilled water was measured after 30 min in an FEK-M photoelectric colorimetric (using a blue light filter No. 3) in cuvettes with distances between the working faces equal to 10 mm.

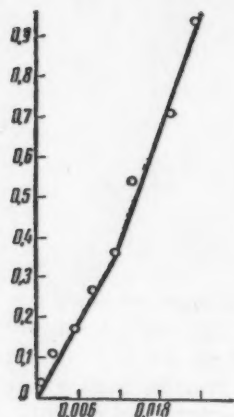


Fig. 1. Optical density of solutions of Pd complex with stannous chloride as a function of Pd concentration.

TABLE 1. Dependence of Optical Density of Palladium-Stannous Chloride Complex Solutions on Acidity of Medium

Concentration of acid, g-eq per liter	Optical density
0.6	0.51
1.0	0.44
2.0	0.35
3.0	0.35
4.0	0.31
5.0	0.35
6.0	0.36

In Fig. 1 the optical density of solutions of palladium with stannous chloride is shown as a function of their palladium concentration. From Fig. 1 it is evident that in the region of low palladium concentrations in the solution a direct relationship is maintained between optical density and concentration. The solutions which are obtained have a stable color, reaching a maximum value in 30 min. We also studied the influence of acidity on color intensity of the palladium complex. The results which were obtained are presented in Table 1.

As it follows from Table 1, the greatest optical density is given by the solution with an acid concentration of 0.6 g-eq/liter. This acid concentration was also adopted in preparing our standard solutions.

The palladium was extracted from the catalyst by means of the following treatment. A 1.00-g sample of catalyst (previously ground in a mortar) was placed in a glass beaker and treated with 5 ml of concentrated HCl (sp. gr. 1.19) and 5 ml of hydrogen peroxide (sp. gr. 1.10) with heating on a steam bath for 15 min; it was then transferred to a 50-ml volumetric flask, and the contents were made up to the mark with distilled water. Subsequently, 5 ml of the solution, filtered through a No. 3 glass filter, was introduced into a 50-ml volumetric flask; 1 ml of 10% stannous chloride solution in concentrated HCl was added, and the contents were made up to the mark with distilled water. After 30 min the solution was measured in the colorimeter, and

the palladium content in the test solution was determined by means of the standard curve. The palladium content in the catalyst was calculated according to the formula

$$\% \text{ Pd} = \frac{cR \cdot 100}{a \cdot 1000} = \frac{c(50 \cdot 10) \cdot 100}{1.00 \cdot 1000} = c \cdot 50,$$

where c is the Pd content in mg/ml, found from the standard curve; a is the weight of the catalyst in grams; R is the dilution, equal to $R_1 \times R_2$, where R_1 is the first dilution and R_2 the second. Results are shown in Table 2 for the determination of palladium content in palladinized gumbrine catalysts, obtained by the method described. The results which were obtained attest to the suitability of our proposed method of analysis for determining the palladium content in palladinized gumbrine catalysts.

TABLE 3. Properties and Composition of Catalyzates of Cyclohexane Obtained on Palladinized Gumbrine Catalysts at 470°, P = 20 atm H₂, v = 1.0 hr⁻¹, and H₂: HC = 5:1

Catalysts	Properties of cata-		Composition of catalyzates of cyclohexane, wt. %									
	n _D ²⁰	d ₄ ⁰	pro-p	iso-bu-	n-butane	iso-pen-	2,2-methyl-	2-methyl-	3-methyl-	mix. of	n-hexane	methyl-
			pane	tane		tane	pentane	pentane	pentane	pentane	pentane	cyclo-
												pentane
												cyclo-
												hexane
												benzene
Activated gumbrine	1,4250	0,7746	—	0,3	0,3	0,6	0,1	Traces	0,3	0,3	0,4	19,5
0,5% Pd - gumbrine	1,4410	0,7958	0,3	0,2	0,4	0,1	0,2	0,2	0,3	0,3	0,4	19,2
0,5% Pd - gumbrine treated with H ₂ S	4,4480	0,7928	0,4	0,4	0,5	0,3	0,2	0,7	0,8	0,8	0,5	22,7
												78,2
												50,2
												28,5
												40,2

TABLE 2. Results of Pd Content Determination in Palladinized Gumbrine Catalysts by Photometric Method

Catalysts	Optical density	Found	
		Pd in mg in 1.00-g sample	Pd content in gumbrine, %
Before catalysts			
0.5% Pd-gumbrine	0,32	5,0	0,5
After catalysts			
0.5% Pd-gumbrine*	0,25	4,2	0,42
0.5% Pd-gumbrine**	0,28	4,5	0,45

* Catalyst was investigated at 470° and 20 atm hydrogen pressure in the cyclohexane dehydrogenation reaction.

** Catalyst was investigated at 330° in the cyclohexane dehydrogenation reaction at normal pressure.

Table 3 shows the properties and composition of the catalyzates of cyclohexane obtained as a result of investigating the activity of the palladinized gumbrine catalyst at 470°, 20 atm hydrogen pressure, v = 1.0 hr⁻¹, and H₂: HC = 5:1.

As is evident from the data of Table 3, the carrier, activated gumbrine, under the conditions which we selected has a considerable isomerizing action; at the same time, its cracking properties are slight. The catalyzate, in addition to unchanged cyclohexane, contains 19.2% methylcyclopentane and 2.2% of C₄-C₆ hydrocarbons. The introduction of a metal possessing dehydrogenating properties onto the carrier results in a dehydrogenation catalyst which is also characterized by pronounced isomerizing properties.

The products of catalysis of cyclohexane in the presence of 0.5% palladinized gumbrine catalyst also contain 19.2% methylcyclopentane and 28.5% benzene. Treatment with hydrogen sulfide leads to a considerable strengthening of both the dehydrogenating and the isomerizing properties of the palladinized gumbrine catalyst. The benzene content in the catalyzate thereby increases from 28.5 to 40.2%, and methylcyclopentane from 19.2 to 22.7%. It should also be pointed out that the cracking ability of this catalyst is almost doubled. Thereby the catalyzates contain propane, isobutane, n-butane, isopentane, n-pentane, 2-methylpentane, 3-methylpentane, cyclopentane, and n-hexane, which are products of hydrocracking the cyclohexane and of hydrogenolysis of the methylcyclopentane (which is formed by cyclohexane isomerization). The increased activity of the palladinized gumbrine catalyst 2 apparently is occasioned by the presence of PdS in it, since precisely this sulfide could be formed in its treatment with hydrogen sulfide. We had obtained similar results previously for rhenium-alumina catalysts treated with hydrogen sulfide [9].

The catalyst, which possesses two selectively marked functions and can carry out simultaneously the reactions of dehydrogenation and isomerization with relatively weak cracking action, may also represent practical interest for carrying out low-octane gasoline upgrading processes.

SUMMARY

1. In the presence of 0.5% Pd - gumbrine catalyst treated with hydrogen sulfide, at 470°, 20 atm H₂, v = 1.0 hr⁻¹, and H₂:HC = 5:1, cyclohexane forms 40.2% benzene and 22.7% methylcyclopentane.
2. The carrier, activated gumbrine, under the same conditions possesses a considerable isomerizing action toward contraction of the six-membered ring to a five-membered.
3. A method has been developed for the photometric quantitative determination of palladium in palladinized gumbrine catalysts.

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DEHYDROGENATION OF n-OCTANE AND 250-320° SYNTHINE FRACTION IN THE PRESENCE OF ACTIVATED WOOL CHARCOAL

E. A. Timofeeva, V. S. Smirnov, and V. I. Bogomolov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

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It has been noted repeatedly in the literature that activated charcoals possess dehydrogenating capability. For example, there are indications that n-pentane in the presence of activated charcoal at 450-500° gives amylenes as the principal product [1]. Moldavskii and co-workers [2] detected 8.2% alkenes, whose structure was not determined, in the condensate obtained from n-octane over wood charcoal at 504° with a space velocity of 0.15 hr⁻¹. On the basis of analytical data on the gases formed (47.6% H₂, 3.9% C₂H₄, 48.5% C₂H₂ + 2) and the results of distilling the catalyzates (about 40% distilled below the boiling point of n-octane), it may be stated that under these experimental conditions there was considerable cracking. Sanford and Friedman [3] studied the reforming of petroleum distillates under the influence of charcoal catalysts. These same catalysts were used in investigating conversions of methylcyclohexane, methylcyclopentane, and n-heptane. On one of the charcoals, promoted with Na₂CO₃, they obtained from n-heptane at 520° an 80% yield of a catalyzate containing 15% alkenes (C₅ and above) and 10% aromatic hydrocarbons. In the opinion of the authors, the alkali additions reinforce the dehydrogenation reaction and reduce the cracking of the hydrocarbons to C₁-C₃.

Rapoport, Nefedov, and Grakhova [4] carried out the contacting of various synthine fractions with charcoal catalysts and came to the conclusion that the reaction of alkane dehydrogenation occurs to a considerable degree in the process of splitting paraffinic hydrocarbons at 450-510°; they note that the reaction of dehydrocyclization to aromatic hydrocarbons is practically absent under these conditions, but no strict proofs are given in the article. Of the results of the experiments conducted with individual alkanes, it was said only that at 470-480° and space velocity of 3 hr⁻¹, on catalyst KAD + 1% NaOH, n-heptane "is subjected only to partial dehydrogenation, without any significant occurrence of the splitting reaction. The noncondensable gases consist 96% of hydrogen." In experiments with cetane, the splitting reaction takes place, along with the dehydrogenation reaction. The hydrogen content in the gas is thereby reduced to 83.5%, the content of saturated hydrocarbons increases to 10.8%, and unsaturated hydrocarbons are also present in the gas. The authors of this investigation emphasize that the unsaturated hydrocarbons formed by dehydrogenation have the double bond in the α -position, on the basis of investigation by the Raman spectra method. Thermodynamic calculations which we arrived at for the dehydrogenation reaction of n-pentane and n-hexane [5, 6] show that under conditions of thermodynamic equilibrium α -olefins cannot be the principal reaction products in the dehydrogenation of these alkanes. There are also experimental data which state that C₅-C₁₀ n-alkanes on dehydrogenation form mainly alkenes with the double bond in the 2, 3, or 4 position [7-12]. All these results were obtained on oxide catalysts. On the other hand, it is well known that in the thermal cracking of paraffinic fractions of petroleum the major portion of the unsaturated hydrocarbons which are formed consists of α -olefins [13].

We set ourselves the task of ascertaining whether it is possible to obtain α -olefins as the bulk product as a result of dehydrogenating n-alkanes in the presence of activated birch charcoal. We took for investigation n-octane and a 250-320° fraction of a synthine obtained on Co-ThO₂-MgO catalyst. As a result of the investigation we were successful in demonstrating with adequate clarity that it is possible to obtain octenes from n-octane on a charcoal catalyst; however, no octene-1 was detected among the octenes by the Raman spectra method. Noticeable quantities of α -olefins were found only in the products of cracking, both of n-octane and of the synthine fraction.

EXPERIMENTAL

The experiments were carried out in the usual flow-type apparatus at atmospheric pressure. The catalyst was activated wood charcoal, grade BAU, treated with hydrochloric acid as indicated in the work of Rapoport and co-authors [4]. Promoted catalyst was obtained by impregnating dried charcoal with sodium hydroxide solution on the

basis of 1 or 5% of the charcoal weight. A 30-ml (7-g) quantity of the catalyst with grain size 1-3 mm was placed in a quartz tube of 22 mm diameter. The length of the catalyst bed was 20 cm. The temperature was measured by a chromel-alumel thermocouple placed in the catalyst bed. The catalyst bed was preheated to the required temperature in a stream of nitrogen before starting the experiment. The starting materials were fed into the tube from an injector by means of a motor. The products of conversion were condensed in a water cooled receiver. After each experiment, a fresh portion of the catalyst was placed in the reactor tube. Refractive index, alkene content by iodine number, and aromatic content by relative dispersion were determined on the catalyzates. Certain catalyzates were analyzed by Raman spectra and also by gas-liquid chromatography. For the latter, an apparatus with microflame detector was used (column length 4 m, stationary phase tricresyl phosphate on kieselguhr, carrier gas hydrogen). An analogous apparatus is described in the work of Kucherov and co-authors [14].

Conversions of n-Octane

The experiments of n-octane dehydrogenation were conducted at 500° and space velocities of 2.0 and 1.0 hr⁻¹ with unpromoted charcoal and with charcoal promoted with 1 and 5% sodium hydroxide. The passage of n-octane over quartz under these conditions gave practically no changes, and no alkenes were detected in the catalyzate. The results which were obtained are presented in Table 1 and in Fig. 1.

TABLE 1. Properties of Catalyzates Obtained from n-Octane at 500° with Space Velocities 2.0 and 1.0 hr⁻¹

Catalyst	Space velocity, hr ⁻¹	Quantity of n-octane passed, ml	Yield of catalyzate, %	n ²⁰ _D	Content of hydrocarbons in catalyzate, %	
					unsaturated	aromatic
BAU	2,0	100	98,5	1,3976	4,1	Her
	1,0	60	90,6	1,3975	8,4	1
BAU + 1% NaOH	2,0	120	93,5	1,3998	11,3	1
	1,0	50	87,2	1,4019	11,1	2
BAU + 5% NaOH	2,0	100	93,7	1,4011	11,4	2
	1,0	40	88,5	1,4029	13,3	5

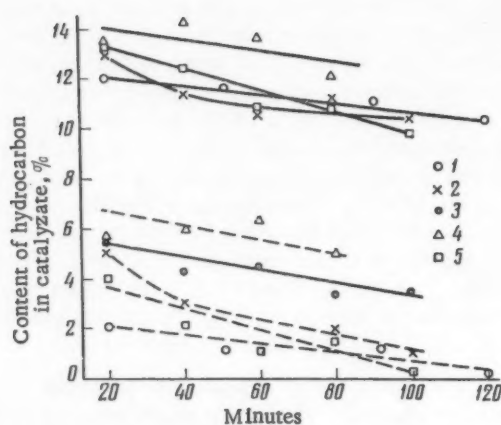


Fig. 1. Change in content of unsaturated (—) and aromatic (---) hydrocarbons in catalyzates, with respect to time: 1) BAU + 1% NaOH, space velocity 2.0 hr⁻¹; 2) BAU + 1% NaOH, space velocity 1.0 hr⁻¹; 3) BAU, space velocity 2.0 hr⁻¹; 4) BAU + 5% NaOH, space velocity 1.0 hr⁻¹; 5) BAU + 5% NaOH, space velocity 2.0 hr⁻¹.

As is evident from the data of Table 1, the promotion of the charcoal by alkali increases considerably its dehydrating capability. At the same time, the quantity of alkali has almost no influence on the yield of catalyzates nor on their alkene content. A larger quantity of alkali in the catalyst increases only the formation of aromatic hydrocarbons. A change in space velocity in the experiments with promoted charcoal is reflected in the yields of catalyzates, which are 6-8% higher at 2.0 hr⁻¹ than at 1.0 hr⁻¹. Moreover, at the lower space velocity approximately twice the amount of aromatic hydrocarbons is obtained. On the unpromoted charcoal a decrease in space velocity leads to a considerable increase in alkene yields.

As shown in Fig. 1, the activity of charcoal catalysts with the passage of time is somewhat decreased and, as a rule, the content of aromatic hydrocarbons in the catalyzates is decreased more rapidly than the content of unsaturates. The duration of one of the experiments conducted on BAU + 1% NaOH at 500° and velocity 2.0 hr⁻¹ was extended to 360 minutes; thereby the content of alkenes in the catalyzate was decreased from 12 to 7%, and the content of aromatic hydrocarbons from 2 to 0%. All of the catalyzates from n-octane (the properties of which

TABLE 2. Properties of Catalysts from Synthine Fraction (space velocity 2.0 hr⁻¹)

Catalyst	Temp., °C	Yield of catalyst, %	n_D^{20}	Iodine number	Content of olefins in catalyst, %
BAU	500	82,5	1,4330	25,6	21,6
BAU+1%NaOH		91,5	1,4357	36,6	30,9
Quartz		91,0	1,4340	14,0	11,8
BAU	525	79,0	1,4335	45,8	33,6
Quartz		84,0	1,4327	22,0	18,6

TABLE 3. Fractional Composition of Initial Synthine Fraction and Catalysts Obtained (space velocity 2.0 hr⁻¹)

Initial synthine fraction or catalyst temperature, catalyst	Content of fractions, %						Residue
	to 250°	250—260°	260—280°	280—295°	195—305°	305—307°	
Initial synthine fraction	1	3	31	31	15	4	15
Catalyzate, 500°, quartz	6	4	27	29	15	6	13
Catalyzate, 500°, BAU	17	5	32	29	12	2	3
Catalyzate, 500°, BAU + 1% NaOH	32	6	28	18	7	5	4
Catalyzate, 525°, quartz	10	5	32	28	13	6	6
Catalyzate, 525°, BAU	40	8	24	16	4	4	4

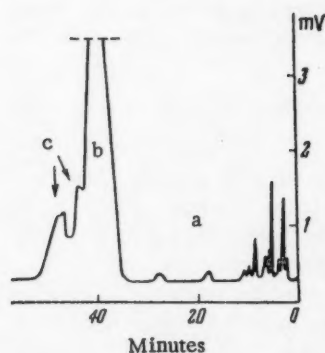


Fig. 2. Chromatogram of catalyst obtained from n-octane on BAU + 1% NaOH at space velocity 2.0 hr⁻¹ (column temperature 35°): a) Cracked products, b) n-octane, c) octenes.

are indicated in Table 1) were analyzed by gas-liquid chromatography; qualitatively, the chromatograms differed little from each other. One of them is shown in Fig. 2. At the 35° column temperature the aromatic hydrocarbons leave the column considerably later, and therefore are not shown on the chromatogram.

For determining the structure of the octenes formed, the catalyst obtained from n-octane at 500° and velocity 2.0 hr⁻¹ on BAU + 1% NaOH was distilled in a 40 theoretical-plate column. The properties of this catalyst were shown in Table 1. A 70 ml sample was taken for the distillation. About 3% cracked products, i.e., fractions boiling 60.0-120.0°, was obtained. On the basis of analysis of this fraction by gas-liquid chromatography, it can be stated that α -olefins (hexene-1, pentene-1) are present in larger quantities than are olefins with other locations of the double bond (hexene-2, pentene-2, and others). The main portion of the catalyst distilled within the boiling range of n-octane and octenes, i.e., at 120-126°; it contained 9% alkenes and about 1% aromatic hydrocarbons. As a result of adsorption of this fraction on silica gel treated with hydrogen peroxide [15], a concentrate was recovered containing 87% octenes (on the basis of iodine number) and 13% n-octane. This same ratio of components is obtained from the chromatograms of the concentrate (Fig. 3). The absence of α -olefins in the concentrate was demonstrated by the Raman spectra method. To all appearances, the bond in

the octenes is located in positions 2 and 3. The presence of octene-4 is also not impossible. The aromatic portion of the catalyst, isolated by adsorption on silica gel (about 1% of the total catalyst) consisted of 12% benzene, 4% toluene, and 84% xylenes and possibly ethylbenzene. The analysis was carried out by gas-liquid chromatography.

Conversions of 250-320° Synthine Fraction

This series of experiments was conducted at 500° and space velocity 2.0 hr⁻¹ on quartz, BAU without promoter, and BAU + 1% NaOH, and also at 525° at the same space velocity on quartz and on BAU without promoter. For each experiment we took 80 ml of synthine fraction, n_D^{20} 1.4360, containing no alkenes (data on distillation of the synthine fraction into narrower fractions are indicated in Table 3).

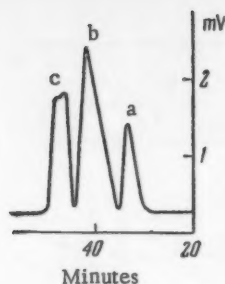


Fig. 3. Chromatogram of octenes concentrate (column temperature 40°): a) n-Octane; b) and c) octenes.

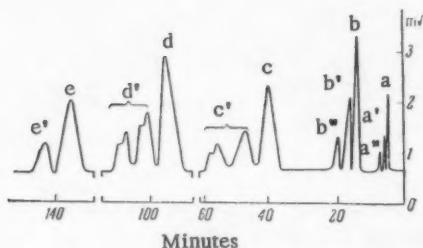


Fig. 5. Chromatogram of reaction products distilling 40-150° obtained from synthine fraction on BAU + 1% NaOH at 500° and space velocity 2.0 hr⁻¹ (column temperature 20°): a) n-Pentane, a') pentene-1, a'') pentene-2; b) n-hexane, b') hexene-1, b'') other hexenes; c) n-heptane, c') heptenes; d) n-octane, d') octenes; e) n-nonane, e') nonenes.

takes place to a greater degree on the unpromoted charcoal, as evidenced by the lower yield of liquid catalyze on the BAU in comparison with the BAU + 1% NaOH (see Table 2). The same phenomenon was noted by Sanford and Friedman in the work cited previously [3]. Figure 4 shows the content of alkenes in the various fractions of the synthine catalyzates. From Fig. 4 it is evident that the use of charcoal catalysts leads to a change in the distribution of alkenes in the fractions. The catalyze obtained on quartz shows a concentration of most of the alkenes in the light fractions, while the catalyzates obtained under the influence of the charcoals show an evenner distribution of the alkenes, even though they remain higher in the light fractions. From Fig. 4 it is also clearly evident that under the influence of promoted charcoal the alkenes formed in all fractions are considerably greater than with the unpromoted charcoal. From the catalyze obtained from synthine at 500° on BAU + 1% NaOH, a 42-150° light fraction was distilled (12% of the total catalyze). The chromatogram of this fraction is presented in Fig. 5. From this chromatogram it follows that α -olefins are present in the cracked products. The synthine catalyzates were not subjected to more detailed analysis, in view of their complex composition.

In conclusion, we take the opportunity to express gratitude to N. I. Shulkin for advice and for the opportunity to carry out the work in the organic catalysis laboratory of the Institute of Organic Chemistry, USSR Academy of Sciences. The Raman spectra were taken by N. S. Andreev, to whom we express gratitude.

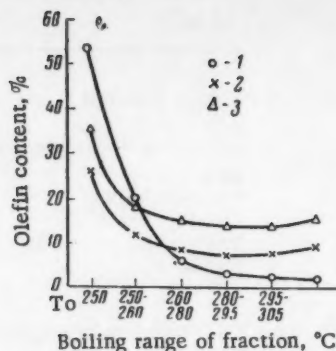


Fig. 4. Content of olefins in fractions of catalyzates obtained on: 1) Quartz; 2) BAU, and 3) BAU + 1% NaOH (temperature of experiments 500°, space velocity 2.0 hr⁻¹).

From the data of Table 2 it is evident that on the unpromoted charcoal the quantity of alkenes formed is approximately twice that formed on quartz, and 10% more alkenes are formed on the promoted charcoal than on the unpromoted. All the catalyzates were distilled from a Favorskii flask into fractions, whose alkene contents were calculated from iodine number determinations, taking into account the average molecular weights of the fractions.

The fractional composition of the catalyzates is shown in Table 3.

As is evident from the data of Table 3, the unpromoted charcoal results in the formation of far more light fractions and less residue (boiling over 307°) than does the quartz. The promoted charcoal, in comparison with the unpromoted, gives twice the amount of fraction boiling up to 250°. However, cracking to gaseous products

SUMMARY

1. An investigation has been made of the reaction of dehydrogenation of n-octane and a 250-320° synthine fraction in the presence of activated wood charcoal.
2. It has been shown possible to carry out with charcoal a practically selective reaction of n-octane dehydrogenation, with a 9% yield of octenes.
3. No octene-1 was detected by Raman spectra in the octenes which were formed. However, α -olefins are present in the cracked products both from n-octane and from the synthine fraction.
4. Promotion of the charcoal by alkali intensifies the cracking reaction of the synthine fraction, thereby increasing the content of alkenes, both in the entire catalyzate and in its individual fractions.

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FREE-RADICAL ADDITION OF DICARBOXYLIC ACID ESTERS TO α -OLEFINE AND THE SYNTHESIS OF α -ALKYLDICARBOXYLIC ACID ESTERS

G. I. Nikishin, Yu. N. Ogibin, and A. D. Petrov

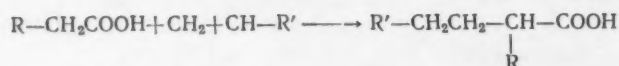
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

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No. 7, pp. 1326-1330, July, 1961

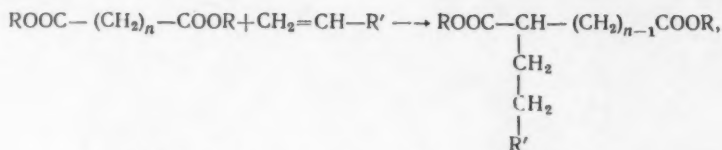
Original article submitted July 14, 1960

We have previously studied the addition of carboxylic acids and their methyl esters of α -olefins [1]:



This reaction proceeds by a free-radical mechanism, the initiator being tert-butyl peroxide between 135 and 200°. Further detailed studies showed that the reaction may be regarded as a new preparative method for dialkylacetic acids. It has a number of advantages over the sodiomalonic and sodioacetoacetic ester syntheses usually employed. The chief advantage is the simplicity of the experimental technique required and the fact that the process takes place in one stage.

The aim of the present work was to extend the applicability of this reaction (free-radical addition of acids to multiple bonds) and to use it for the synthesis of α -alkyldicarboxylic acid esters. It was established that malonic, succinic, adipic, azelaic, and sebacic acid esters add on the α -olefins with the formation of the corresponding α -alkyldicarboxylic acid esters:



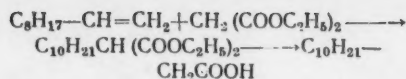
where $n = 1, 2, 4, 7, 8$; $R=CH_3-$; C_2H_5-

The reactions were carried out at atmospheric pressure in the presence of tert-butyl peroxide. The conditions employed in the various experiments, the proportions of the reagents and of the peroxide, and the yields of the 1:1 adducts are given in Table 1, and the properties of the 1:1 adducts in Table 2. All the experiments were carried out under comparatively similar conditions — duration 4-6 hr, at 155-165°, and with ester:olefin:peroxide ratios of 7.7-10:1:0.25-0.26. The 1:1 adducts with the exception of those of α -olefins and methyl adipate (experiments 4 and 5), were obtained in high yields (52-75%). In the case of methyl adipate the yields were much lower. To confirm the structure postulated for the 1:1 adducts (experiments 4-7), dimethyl α -octyladipate (experiment 4) was hydrolyzed to the free acid (m. p. 74.5-75°), which was then converted to the amide (m. p. 186.2-186.8°). Published data [2]: α -octyladipic acid, m. p. 75°; α -octyladipamide, m. p. 186.7°.

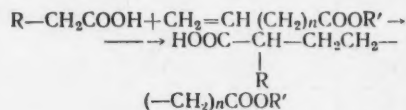
The data obtained here and in previous work [1] may thus be regarded as proof that the addition of dibasic acid esters to α -olefins takes place at the α -carbon atom of the former. We have already reported that only those acids or esters which have the CH_2 or CH group in the acid radical can add on readily to α -olefins. Methyl acetate could not be added to 1-decene, i.e., it was impossible to convert the olefin to an acid having two additional carbon atoms in the molecule. This was successfully accomplished in another way. By adding dimethyl malonate to 1-decene, diethyl decylmalonate was obtained. The latter, after hydrolysis and decarboxylation, yielded lauric acid;

TABLE 1

Expt. No.	Reactants		Quantities used in reaction, moles				Yield of 1:1 adduct		Residue, g
	Ester or acid A	unsaturated compound B	A	B	tert-butyl peroxide	Temp., °C	Time, hr	g	%
1	CH ₃ (COOC ₂ H ₅) ₂	1-Decene	1.6	0.16	0.04	155-160	4	36	75
2	CH ₃ (COOC ₃ H ₇) ₂	4-Methyldec-1-ene	2.0	0.2	0.05	155-160	4.5	43	68.4
3	CH ₃ COOC(CH ₃) ₂ COOCH ₃	1-Octene	1.2	0.156	0.041	160-168	5.5	27	67
4	CH ₃ COOC(CH ₃) ₂ COOCH ₃	1-Octene	1.8	0.235	0.061	152-155	6	27.6	42
5	CH ₃ COOC(CH ₃) ₂ COOCH ₃	1-Decene	1.2	0.156	0.041	158-163	5	19.5	38.5
6	CH ₃ COOC(CH ₃) ₂ COOCH ₃	1-Octene	1.2	0.156	0.041	160-165	5	26.6	52
7	CH ₃ COOC(CH ₃) ₂ COOCH ₃	1-Octene	1.2	0.143	0.04	158-162	5	26.7	54.5
8	n-C ₈ H ₁₇ COOH	Methyl acrylate	3.0	0.3	0.075	158-160	6	11.7	18
9	n-C ₆ H ₁₃ COOH	Methyl acrylate	4.0	0.2	0.1	156-162	4	14.7	34
10	n-C ₉ H ₁₉ COOCH ₃	Methyl acrylate	2.0	0.2	0.05	157-162	5	16.3	30
11	n-C ₄ H ₉ COOH	Methyl undecenoate	2.4	0.312	0.082	160-165	6	49	52.5



The esters of α -alkyl dicarboxylic acids can also be obtained by the addition of monobasic acids or their esters to unsaturated acids or their esters:



The reaction was carried out in three cases (experiments 8-11). Enanthic acid and methyl caprate were added to methyl acrylate ($n = 0$), and valeric acid was added to methyl undecenoate ($n = 8$). A high yield of the 1:1 adduct with methyl acrylate could not be obtained. This is obviously due to the ease of polymerization and telomerization under the reaction conditions, since, in addition to the small yield of the 1:1 adduct, a large quantity of macromolecular products is obtained (see column headed "residue" in Table 1). To increase the yield of the 1:1 adduct of methyl acrylate and enanthic acid, a 20:1:0.5 acid: methyl acrylate: peroxide ratio was employed in experiment 9 instead of the usual 10:1:0.25 (experiment 8). However, the yield was not much improved. The yield of the addition product of valeric acid and methyl undecenoate is close to those of the 1:1 adducts of monobasic acids and α -olefins under analogous conditions. The appropriate melting points, or more correctly the temperatures of the appearance of liquid phase, of α -alkyldicarboxylic acid esters, which are liquid at room temperature, were determined. The determinations were made in a test tube 20 mm in diameter mounted in another vessel ("jacket"). Seven ml of ester was placed in the test tube and a thermometer was inserted. On cooling the esters turned into a crystalline mass; the cooling was then terminated and the temperature at which liquid phase appeared in the test tube, inclined at 45°, was noted. The following results were obtained: dimethyl ester of α -octylsuccinic acid, -9 to -10°; dimethyl ester of α -octylazelaic acid, 1.5°; dimethyl ester of α -octylsebacic acid, 1 to 0°; dimethyl ester of α -decyladipic acid, 7.5°; diethyl ester of decylmalonic acid, -10°.

For compounds of the type $\text{CH}_3\text{OOCCH}(\text{C}_8\text{H}_{17})(\text{CH}_2)_m\text{COOCH}_3$ (Experiments, 3, 4, 6, 7, and 10) exaltation of molecular refraction (ΔMR_D) was observed, the average value of ΔMR_D being -0.6.

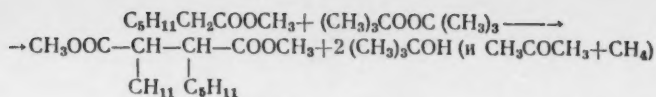
Kharasch and Gladstone [3] converted monobasic acids to the dibasic under the influence of acetyl peroxide; they showed that decomposition of acetyl peroxide in acetic, isobutyric, and chloroacetic acids leads to condensation of the α -carbon atom with the formation of succinic, tetramethylsuccinic, and dichlorosuccinic acids, respectively, in 42-45% yields, based on the peroxide. The present investigation established that a condensation of this type takes place readily also under the influence of tert-butyl peroxide. The methyl ester of enanthic acid yielded the dimethyl ester of α,α' -dipentylsuccinic acid in 36% yield, based on the peroxide:

TABLE 2

Expt. No.	1:1 Adduct	Mol. wt.		B. P., °C., mm Hg	d_4^{20}	n_D^{20}	MR		Found, %		Calc., %	
		found*	calc.				found	calc.	C	H	C	H
1	$C_{10}H_{21}CH(COOC_2H_5)_2$			148-150 2	0,9373	1,4377	84,09	84,58				
2	$C_6H_{13}-CH-(CH_2)_3CH(COOC_2H_5)_2$ CH_3			132-135 1,5	0,9337	1,4392	88,62	89,22	68,51 68,40	10,90 10,79	68,75	10,90
3	$CH_3OOC-CH-CH_2COOCH_3$ C_8H_{17}	253,7	258,35	133-135 1,5	0,9679	1,4392	70,23	70,62	64,95 64,80	10,01 9,82	65,08	10,15
4	$CH_3OOC-CH-(CH_2)_3-COOCH_3$ C_8H_{17}	281	286,4	153-154 1,5	0,9576	1,4431	79,30	79,93	66,83 66,63	10,50 10,51	67,09	10,56
5	$CH_3OOC-CH-(CH_2)_3COOCH_3$ $C_{10}H_{21}$			170-172 2	0,9446	1,4461	88,79	89,22				
6	$CH_3OOC-CH-(CH_2)_4COOCH_3$ C_8H_{17}			159-159,5 1,5	0,9406	1,4462	93,17	93,87	69,24 69,35	11,10 10,90	69,46	11,05
7	$CH_3OOC-CH-(CH_2)_7COOCH_3$ C_8H_{17}			169,5-170 1,5	0,9363	1,4472	97,78	98,42	69,96 69,75	10,98 10,83	70,13	11,18
8	$CH_3OOC-CH_2CH_2-CH-COOH$ C_8H_{17}	220,7	216,27	155-157 1,0	1,0281	1,4482	56,33	56,57	61,06 61,08	9,10 9,38	61,08	9,32
10	$CH_3OOC-CH_2CH_2-CH-COOCH_3$ C_8H_{11}			128-130 1,0	0,9666	1,4435	74,78	75,28	66,35 66,55	10,50 10,20	64,14	10,36
11	$CH_3OOC-(CH_2)_{10}-CH-COOH^{**}$ C_8H_{17}	300,9	300,43	190-192 1,0					67,93 68,00	10,59 10,53	67,96	10,74

* The molecular weights were calculated from acid and ester numbers.

** M. p. 36.5-37.5° (recrystallized from acetone).



EXPERIMENTAL

All the experiments described in Table 1 were carried out by the same method. The ester or the acid itself (component A) was placed in a flask provided with a thermometer, a dropping funnel, a reflux condenser, and a stirrer. A solution of tert-butyl peroxide and of the unsaturated compound (component B) in approximately 1/4 to 1/3 of the total quantity of component A calculated for the reaction was added dropwise to the main bulk of the ester, which had been heated to 155-165°; the time of the addition is given in the table. After the addition had been completed, the mixture was stirred for a further hour at the reaction temperature and then distilled. Broad fractions of 1:1 adducts were separated and further purified by fractional distillation. The residue in the distillation flask consisted of higher-boiling products (see column headed "residue" in Table 1).

Experiment 1. Diethyl decylmalonate was converted to the decylmalonic acid by being boiled with 50% KOH and subsequent treatment with concentrated hydrochloric acid. The free acid decarboxylated on heating, yielding lauric acid; m. p. 43.5-44°.

Experiment 2. Similarly, diethyl 4-methyldecylmalonate was converted to 6-methyldodecanoic acid; m. p. 156-158° (1.5 mm); d_{20}^{20} 0.8926, n_D^{20} 1.4442; MR found 63.81; MR calc. 63.91. Found: C 72.86, 72.95; H 12.08, 12.20%; mole wt. 215.2 (from the acid number). $\text{C}_{13}\text{H}_{26}\text{O}_2$. Calculated: C 72.84; H 12.23%; mole wt. 214.35. The yields of the acids in experiments 1 and 2 were approximately 80%.

Experiment 4. Hydrolysis under the conditions of experiment 1 of 9 g of dimethyl α -octyladipate gave 5.6 g (yield 75%) of α -octyladipic acid melting at 74.5-75.0° (after 3 recrystallizations from acetone). A mixture of 1 g of the acid and 10 ml of thionyl chloride was heated to boiling for approximately 1 hr; the excess thionyl chloride was then distilled off, and the residue was treated with aqueous ammonia. The diamide of α -octyladipic acid formed melted at 186.2-186.8° after recrystallization from 70% alcohol. Published data [2]: m. p. of acid 74.5-75°; m. p. of the amide 186.7°.

Recomposition of tert-Butyl Peroxide in Methyl Enanthate

A solution of 20 g (0.137 mole) of the peroxide in 50 g of the ester was added, over 5 hr, to 80 g of the enanthic acid ester heated to 145-155°. Yield 14 g (36%) of the dimethyl ester of α,α' -dipentylsuccinic acid; b. p. 108-110° (1 mm); d_{20}^{20} 0.9527, n_D^{20} 1.4420; found MR 79.54; calc. MR 79.93. Found: C 66.76, 66.89; H 10.30, 10.31%. $\text{C}_{16}\text{H}_{30}\text{O}_4$. Calculated: C 67.10; H 10.56%.

SUMMARY

1. Free-radical addition of dicarboxylic acid esters to α -olefins leads to the formation, in high yields, of α -alkyldicarboxylic acid esters. The reaction may be employed for the preparative synthesis of α -alkyldicarboxylic acids.

2. Carboxylic acids (or their esters) add on to esters of unsaturated acids with the formation of dicarboxylic acid esters.

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POLYMERIZATION AND COPOLYMERIZATION OF N-VINYL COMPOUNDS

COMMUNICATION 8. POLYMERIZATION OF VINYLSUCCINIMIDE IN AQUEOUS SOLUTION

A. F. Nikolaev, S. N. Ushakov, and N. V. Daniel'

Lensoviet Leningrad Institute of Technology

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In our previous communication [1] we showed that vinylsuccinimide readily polymerizes under various conditions (in block, water, and organic solvents) into a macromolecular compound which is insoluble in the available solvents, undergoing pronounced swelling in most of them (dichloroethane, methylene chloride, chloroform, pyridine, etc.). It has been suggested that polymerization is accompanied by secondary processes leading to polymeric-chain branching and partial cross-linking.

Soluble polymers may be obtained by the polymerization of vinylsuccinimide in solution (for example in dichloroethane) in the presence of an active chain-transfer agent — fluorene. However, under these conditions a polymer of relatively low molecular weight is formed (intrinsic viscosity $[\eta] = 0.39$). Polymerization of vinylsuccinimide in aqueous solution, even with considerable dilution, does not give soluble polymers. This work continues the investigation of vinylsuccinimide polymerization in aqueous solution in the presence of a soluble initiator — potassium persulfate. The polymer chain length was controlled and the cross-linking was prevented by the addition of formaldehyde (as formalin) and urea. The reaction temperature was maintained at 70 and 80°. In all the experiments a 10% aqueous solution of vinylsuccinimide was employed. The polymerization reaction was continued until the extent of conversion attained was 95-98%.

Effect of Stirring and Atmospheric Oxygen on the Polymerization of Vinylsuccinimide

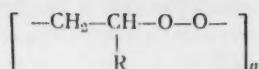
Experiments on the polymerization of vinylsuccinimide under static conditions and with stirring have shown that hydrodynamic conditions have a pronounced effect on the rate of the process. When the reaction is carried out with vigorous stirring, polymerization is completely inhibited, and with weak stirring the rate is very low; only in the absence of stirring the reaction proceeds rapidly at 70-80°, at initiator concentrations greater than 0.2%. A similar effect of stirring on the rate of the heterogeneous polymerization without an emulsifier was observed with methyl methacrylate [2] and acrylonitrile [3]. Experiments on the polymerization of vinylsuccinimide with stirring in an atmosphere of nitrogen have shown that the formation of polyvinylsuccinimide proceeds normally, as in the polymerization under static conditions. This shows that it is the atmospheric oxygen which under the given conditions inhibits the polymerization when the mixture is stirred. Clearly, stirring causes increased absorption of oxygen from the air, at a rate which is greater, the greater the rate of stirring.

The oxygen absorbed by the medium, water for example, combines with the monomer. In our view addition of oxygen to an unsaturated compound will proceed faster, the greater the charge on the double bond, i.e., the more it is polarized,

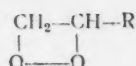


On theoretical grounds the monomers mentioned above may be arranged in the following order with respect to the magnitude of the positive charge on the double bonds: acrylonitrile > methyl methacrylate > vinylsuccinimide.

As a result of chemical reaction between the unsaturated compound and oxygen, peroxy compounds are formed, which lead to the formation either of soluble polymeric peroxides of the general form



or of peroxy compounds of the following structure [4]:



Polymeric peroxides are known for acrylonitrile [5] and styrene [6, 7]. Decomposition of peroxy compounds takes place at different temperatures, depending on the nature of the monomer. If the peroxide formed is unstable under the conditions of the polymerization, the prolonged induction period is not observed, and in certain cases the reaction is accelerated. When the compounds are stable, atmospheric oxygen inhibits the process. Thus it may be expected that when the peroxide of the monomer is capable of decomposition, polymerization should not be inhibited by oxygen at higher temperatures. In fact, at 80-90° the polymerization of vinylsuccinimide proceeds rapidly at any rate of stirring, whereas at lower temperatures formation of polymer is not observed.

Effect of Added Formalin and Urea on the Polymerization of Vinylsuccinimide

Addition of 16% or more of formalin and 10% and more of urea to vinylsuccinimide leads to the formation of a polymer soluble in chlorinated hydrocarbons, particularly in methylene chloride and chloroform. This amount of formalin slows down somewhat the rate of polymerization, whereas the urea increases it slightly in comparison with the polymerization of vinylsuccinimide under static conditions without chain-transfer agents. At lower concentrations of the additive, polyvinylsuccinimide formed remains soluble. The table gives the experimental data for the polymerization of vinylsuccinimide in aqueous solution in the presence of potassium persulfate and formalin or urea.

Polymerization of Vinylsuccinimide in Aqueous Solution in the Presence of Potassium Persulfate

Initiator concentration, % of monomer	Chain-transfer agent	Concentration of chain transfer agent, % of monomer	Polymerization temperature, °C	Polymerization time, min
0,1	Urea	10	80	55
0,2	"	10	70	80
0,3	"	10	70	65
0,3	"	10	80	30
0,1	Formalin	16	80	210
0,2	"	16	70	260
0,3	"	16	70	200
0,3	"	16	80	120

Gregg and Mayo [8] showed that when the catalyzed polymerization reaction takes place under conditions such that the concentration of the monomer and initiator are changed little, whereas that of the chain-transfer agent decreases considerably, the transfer constant may be determined from the following equation:

$$\frac{1}{P} = \frac{1}{P_0} + C \frac{[S]}{[M]}$$

where P_0 is the degree of polymerization in the absence of the transfer agent; P is the degree of polymerization in the presence of the transfer agent; C is the transfer constant, given by the ratio of the constant for the interaction between the polymeric radical and solvent to the polymer chain-propagation constant; M is the concentration of the monomer; S is the concentration of the transfer agent.

When the transfer constant is greater than unity, the concentrations of transfer agent necessary to produce a marked reduction in chain branching and to prevent cross-linking are small. Although lack of equations for the calculation of the molecular weight of polyvinylsuccinimide has so far made it impossible to calculate the absolute value of the transfer constants, it is nonetheless possible to conclude that they must be less than unity in the case

of formalin and urea for vinylsuccinimide radicals (because of the large quantities of water-soluble chain-transfer agents which have to be introduced into the reaction mixture). The necessity for transfer agents in the polymerization of vinylsuccinimide shows that the polymeric vinylsuccinimide radical is very reactive; as a result chain transfer can take place via the polymer. The solubility of the polymers is improved when the reaction temperature is raised from 65 to 80°. This is due to the lower molecular weight of the polymers formed.

Effect of the Potassium Persulfate Concentration on the Polymerization of Vinylsuccinimide

In the presence of potassium persulfate, polymerization of vinylsuccinimide in aqueous solutions takes place rapidly and goes to completion. With increase in the initiator concentration, the yield of polyvinylsuccinimide and the reaction rate also increase. Figures 1 and 2 show the variation of the vinylsuccinimide polymerization rate with the square root of the initiator concentration. The data obtained indicate a high polymerization rate both at 70° and at 80°; in all cases the variation with \sqrt{C} is linear.

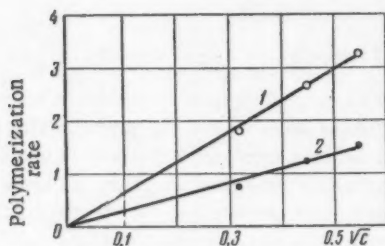


Fig. 1. Dependence of the rate of polymerization of vinylsuccinimide in the presence of urea on the square root of the initiator concentration: 1) 80°; 2) 70°.

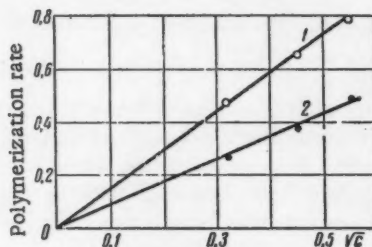
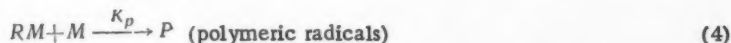


Fig. 2. Dependence of the rate of polymerization of vinylsuccinimide in the presence of formalin on the square root of the initiator concentration: 1) 80°; 2) 70°.

Examination of the factors affecting polymerization of vinylsuccinimide in an aqueous medium leads to several conclusions: 1) The water soluble initiator breaks down in water to primary radicals; some recombine but the majority are captured by the vinylsuccinimide; 2) polymerization of vinylsuccinimide requires highly effective initiation; 3) polyvinylsuccinimide is precipitated from solution during the reaction without affecting the viscosity of the reaction medium; 4) the over-all polymerization rate is proportional to the square root of the initiator concentration not only in the initial stage but also at more advanced stages of the monomer conversion.

The observed relations can be conveniently analyzed by means of the following schematic representation of the individual stages of the polymerization:



where I is the initiator; R and RM are the primary and initial polymeric radicals; M is the monomer; K' , K_0 , K_i , K_p , and K_t are the constants for the initiator decomposition, for the interaction of the initiating radicals, and for the propagation and termination of the polymeric radicals, respectively.

Since the great majority of the radicals R arising in the decomposition of potassium persulfate initiate the polymerization of vinylsuccinimide, we can write

$$K' [I] \gg K_0 [R]^2 \quad (6)$$

Hence from Eq. (1) and (3) we have

$$K' [I] = 2K_i [R] [M] \quad (7)$$

and from Eqs. (3), (4), and (5)

$$2K_i [R] [M] = 2K_p [RM] [M] = K_t [P]^2 \quad (8)$$

According to Eq. (4), the over-all rate of polymerization may be written in the form

$$V_{\text{total}} = K_p [RM] [M] \quad (9)$$

However, from Eqs. (7) and (8), it follows that

$$K' [I] = K_t [P]^2, \quad (10)$$

whence

$$[P] = \left[\frac{K_t [I]}{K_t} \right]^{1/2} \quad (11)$$

and, consequently,

$$V_{\text{total}} = \frac{K_p (K')^{1/2} [I]^{1/2} [M]}{(K_t)^{1/2}} \quad (12)$$

when

$$K_1 = \frac{K_p (K')^{1/2}}{(K_t)^{1/2}} \quad (13)$$

$$V_{\text{total}} = K [I]^{1/2} [M] \quad (14)$$

The over-all rate of polymerization is proportional to the concentration of the monomer and to the square root of the initiator concentration. The experimental data confirm this conclusion for the range of the potassium persulfate concentrations studied, 0.1 to 0.3% with respect to vinylsuccinimide. It may be supposed that at increasing initiator concentrations the recombination of the radicals [Eq. (2)] and the destruction of the growing polymeric radicals through their interaction with the primary radicals R would take place to an ever increasing extent. The molecular weight of the polyvinylsuccinimide may vary in relation to the conditions under which it is obtained. In our experiments the intrinsic viscosity varied from 0.7 to 1.4. The polymers obtained in the presence of urea have a higher viscosity than those obtained in the presence of formalin. The rate of polymerization of vinylsuccinimide is greatly affected by an admixture of β -acetoxyethylsuccinimide (starting material for the preparation of the monomer). Its presence in an amount of 1% completely prevents the formation of the polymer.

EXPERIMENTAL

The synthesis and purification of vinylsuccinimide have already been described [9]. Potassium persulfate was analyzed by methods described for the determination of peroxy compounds [10]. Vinylsuccinimide was polymerized in a flask fitted with a stirrer and a mercury seal, a reflux condenser, and a thermometer. In a number of experiments the reaction was carried out in an atmosphere of nitrogen or without stirring. When additives (formalin and

urea) were employed, they were added, after analysis, into a 10% solution of vinylsuccinimide before raising the temperature in the thermostat. The properties of the materials employed (vinylsuccinimide, urea, formalin, potassium persulfate) agreed with the published data. Vinylsuccinimide melted at 48.5° and its purity was 99.5%, the urea conformed to GOST 2081-57, formalin to GOST 1625-54, and potassium persulfate to GOST 4146-48.

The temperature of the polymerization reaction was maintained to ± 0.2 . As the reaction proceeded, the polyvinylsuccinimide formed precipitated out of the reaction mixture, first as a finely dispersed powder, uniformly distributed throughout the aqueous medium, and then as lumpy masses settling to the bottom of the flask. The rate of the reaction and the yield of the polymer were determined by brominating samples taken at intervals from the flask. The unreacted monomer was analyzed by the bromide - bromate method in the presence of hydrochloric acid. The polyvinylsuccinimide was freed from traces of unreacted monomer, initiator, and additives by prolonged washing (stirring in the flask), repeated three times, with distilled water heated to 80°. The washed polymer was dried to constant weight in vacuum oven at 60° (10 mm) or in an ordinary oven in air at 60-70°. The method used for the determination of the solubility of polyvinylsuccinimide has been described [11]. The intrinsic viscosity of the polymer was determined from the relative viscosity of 0.1% solutions in dichloroethane or methylene chloride [12].

SUMMARY

1. It has been established that polymerization of vinylsuccinimide in aqueous solution in the presence of potassium persulfate can yield polymers of high molecular weight, and soluble in readily available solvents; chloroform, methylene chloride, dichloroethane, dioxan, pyridine, etc. Formalin and urea are suitable as additives for suppressing the branching and cross-linking of the polymeric chains.

2. Polymerization of vinylsuccinimide in aqueous solution is strongly inhibited by atmospheric oxygen, especially below 70°.

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CATALYTIC HYDROPOLYMERIZATION OF OLEFINS AND THEIR HYDROCONDENSATION WITH CARBON MONOXIDE

Ya. T. Eidus

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR
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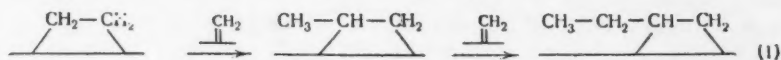
Catalytic reactions in which carbon monoxide is reduced with hydrogen may involve either pure reduction with the formation of molecules containing one carbon atom or condensation-polymerization with the formation of new carbon-carbon bonds. Complete reduction of CO to CH₄ in the methanol process belongs to the first type and the reactions of CO and H₂ to form ethylene (Orlov method), Synthol, Synthine, Synol, and isosynthesis hydrocarbons belong to the second. A number of reactions based on the ternary mixture of olefins, carbon monoxide, and hydrogen also involve condensation, for example the formylation of olefins in the oxo synthesis at 150-300 mm and 200° in the presence of cobalt hydrocarbonyl as catalyst. The reaction in which carbon monoxide undergoes catalytic hydrocondensation with olefins at atmospheric pressure, 190-200°, and in the presence of precipitated cobalt catalysts, discovered by the present author together with Puzitskii, also belongs to this type.

The data which helped to establish the nature of the hydrocondensation of CO with olefins followed from some of the results obtained by the present author in an investigation of the mechanism of the reaction in which hydrocarbons are formed from CO and H₂. The most important of these was the experimental confirmation of the intermediate formation of methylene radicals, in this reaction, on the cobalt catalyst surface, as shown by the partial methylation of benzene to toluene by a mixture of CO and H₂ [1]. The methylation was effected by the products of the incomplete reduction of CO — methylene radicals. Recently, Chinese investigators [2] confirmed these results for the cobalt catalyst and for the first time methylated benzene into toluene also over an iron-copper catalyst.

After Fischer's carbide theory postulating the formation of CH₂ radicals from carbides resulting from the interaction between CO and group VIII metal catalysts was proved erroneous, the present author suggested, on the basis of studies of the behavior of oxygen-containing compounds on a cobalt catalyst, that CO undergoes stepwise reduction into the methylene radical via the hydroxymethylene radical (CHOH) [3]. In isosynthesis on dehydration catalysts (Al₂O₃, ThO₂) hydroxymethylene radicals, formed by the semicatalytic hydrogenation of CO, give rise to side chains in the final hydrocarbons [4].

The hypothesis of the doublet stepwise mechanism of the polymerization of CH₂ radicals in the synthesis of hydrocarbons from CO and H₂ [5] has played an important role in the discovery of the hydrocondensation reaction. This hypothesis, unlike that of the polymerization of CH₂ radicals into a "giant molecule" [6], is consistent with the requirement of geometric correspondence of the multiplet theory [7] and with the principle of preservation of the valence angle in catalysis and adsorption [8]. These considerations have suggested the possibility of polymerizing olefins with methylene radicals on a cobalt catalyst. This has been confirmed experimentally and has led to the discovery of the hydrocondensation reaction of CO with olefins [9].

It might have been supposed that the reaction involves successive methylation of the initial olefin and the formation of its higher homologs:



However, this mechanism predominates only at relatively high CO concentrations in the olefin — hydrogen mixture. At low concentrations of CO, however, the amount of hydrocarbons formed is greater than expected from the CO

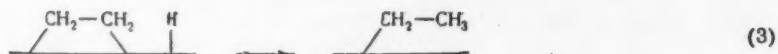
reacted. The explanation is that under these conditions another, hitherto unknown process takes place — hydropolymerization of the olefin under the action of small quantities of CO in the presence of H₂ [10]. This reaction and the hydrocondensation of CO with olefins take place simultaneously, one passing into the other, depending on the conditions, in particular on the proportions of the components in the initial mixture. They are accompanied by a number of other processes which affect the nature and composition of the reaction products, for example hydrogenation of the olefin into the paraffin with the same number of carbon atoms in the molecule, displacement of the double bond in the olefin molecule, etc.

Hydrocondensation and hydropolymerization reactions of olefin make possible the synthesis of higher aliphatic hydrocarbons, predominantly of straight-chain structure, with a large range of molecular weights. The reaction products are formed mainly from the initial olefin and contain considerable proportions of higher olefins, which are greater the lower the molecular weight of the initial olefin and the lower the hydrogen content in the initial mixture. These higher olefins are valuable intermediates for organic synthesis, for example for the formation of flotation reagents, plasticizers, and surface-active and wetting agents. Thus the present author synthesized alkyl sulfates, alkylbenzene-sulfonates (high-grade wetting agents) [11] from various fractions of products resulting from the hydrocondensation of carbon monoxide with ethylene and propene. The method of alkoxycarbonylation of olefins by means of CO, developed by the present author, has yielded carboxylic acids with doubly methylated quarternary carbon atoms in the α -position to the carboxyl group [12].

Hydrocondensation of carbon monoxide with olefins and hydropolymerization of the latter under the influence of small quantities of CO acquired particular theoretical interest when the role of active surface intermediates and the possibility of chain processes in heterogeneous catalysis became apparent. Much still remains to be done before these questions are elucidated experimentally, despite the available theoretical ideas on heterogeneous catalytic chain reactions [13]. Results obtained by the present author in studies of reactions in olefin — CO — H₂ mixtures suggest the formation of active intermediates on the catalyst surface. These are methylene and alkyl radicals formed by incomplete reduction of carbon monoxide with hydrogen,



by the semihydrogenation of olefins,



and finally by the hydrogenolysis of hydrocarbon species. Once formed, these intermediates exert a specific effect on the reaction and on the composition of the final products.

Hydrocondensation of Carbon Monoxide with Olefins

In reactions of this type the CO — H₂ mixture behaves as an alkylating, and in particular as a methylating, agent leading to the formation of higher homologs of the olefins. This reaction is selective with respect to the cycloolefins. Thus when cyclohexene is allowed to react with a mixture of CO and H₂ at 190° on a cobalt catalyst, its mono- and 1,2-dimethyl derivatives are obtained in 10% yield [14]. Mono-, di-, and trimethyl derivatives of cyclopentadiene have been obtained in this way [15]. Alkylation of cyclopentene under these conditions has resulted in 33% yield, with respect to the initial CO, of products which after complete hydrogenation contained 45% of methylcyclopentane, 20% of ethylcyclopentane, 8% of propylcyclopentane, 10% of cyclohexene, 10% of methylcyclohexane, and 7% of ethylcyclohexane. The enlargement of the 5- to the 6-membered ring is directly connected with the alkylation process [16].

Hydropolymerization of Olefins in the Presence of Hydrogen Under the Influence of Small Quantities of Carbon Monoxide

This reaction accompanies the hydrocondensation of CO with aliphatic olefins. Carbon monoxide exhibits a new property in the hydropolymerization reaction: In small quantities and in the presence of H₂ it behaves as an initiator of the hydropolymerization of aliphatic α -olefins. At the same time it actually participates in the reaction, its oxygen being converted to water. Cycloolefins with a double bond in the ring do not enter into this reaction as they do not belong to α -olefins. Apart from the true polymers and their hydrogenated derivatives, polymers which are not multiples of the initial olefin are also formed in the hydropolymerization. Table 1 gives the proportions of

the methylation products, polymers which are and which are not multiples of the initial olefin, obtained from equimolar olefin - H₂ mixtures containing 5% CO.

TABLE 1

Initial olefin	Hydrocarbon content of hydrocondensate, vol. %						
	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉
Ethylene [10]	8	20	12	19	16	13	9
Propene [17]	—	10	14	20	14	13	11
1-Butene [12]	—	—	24	15	8	9	8
1-Pentene [19]	—	—	—	20	10	7	10

TABLE 2

CO, %	Total yield of hydropolymerization product, ml/m ³	Oil: gasoline: gas-oil
0.00	0.0	0:0:0
0.06	39	0:1:1.3
0.1	81	0:1:0.8
0.5	165	0:1:0.9
1.5	311	0.07:1:1.0
4.0	297	0.2:1:0.3
6.1	323	0.3:1:0.4

TABLE 3

CO,	0.1	0.5	4.6	15-20	5.7	6.2	11.6	15.4	18
Yield with respect to initiator	44	22	8	4	3.7	3.7	0.7	0.2	0.1
	For ethylene				For propene				

Table 1 shows that hydrocondensates of ethylene and propene contain 8-10% of the methylation products (C₃ and C₄ fractions respectively) and the hydrocondensates of butene and pentene contain 20-24%; the remainder consists of hydropolymerization products. As an example, data for the hydropolymerization of ethylene are given in greater detail. Ethylene in an equimolar mixture with hydrogen containing 5% CO undergoes conversion to the extent of 80-95%. The reacted ethylene is 20% hydrogenated to ethane and 80% passes into the liquid hydropolymerization product. The yield of the latter amounts to 500 ml per m³ of the initial gas or 50 ml/liter-hr⁻¹, which is five times more than the yield in the synthesis of hydrocarbons from carbon monoxide and hydrogen under the same conditions. The hydropolymerization product contains 70% of higher olefins. Under the same conditions neither ethylene nor its mixture with CO react, whereas an ethylene mixture with hydrogen gives only ethane. Consequently the hydropolymerization of ethylene in its mixture with hydrogen is initiated not by CO itself but the active intermediate formed on the catalyst surface as a result of incomplete reduction of CO.

Concentration of Carbon Monoxide

The concentration of CO in the initial gas mixture strongly affects the course of the reaction and the composition of its products [10]. In complete absence (< 0.01%) of CO ethylene does not undergo hydropolymerization at all; the reaction does proceed to some extent, however, at very small concentrations (several hundredths percent) of CO. Table 2 shows the effect of the CO concentration on the over-all yield of higher hydrocarbons and on proportions by volume of oil, gasoline, and gas-oil (C₃ - C₄) in the hydropolymerization product obtained from an equimolar ethylene - hydrogen mixture. The volume fraction of gasoline was taken as unity.

Table 2 shows that as the CO concentration is increased to 6%, there is a continuous increase in the over-all yield of the hydropolymerization product. At the same time the molecular weight of the ethylene polymers also becomes greater: Initially the gas-oil fraction predominates, then gasoline, and finally the oil fraction appears and increases in extent. When the CO concentration is increased to 15%, the over-all yield falls in experiments with propene and butene, but not with ethylene. A characteristic feature of the hydropolymerization of olefins is that the number of the olefin molecules taking part in the reaction for each CO molecule which has reacted ("yield with respect to initiator") may be greater than unity, reaching several tens, and falls with increase in the CO concentration (Table 3) [20]. These relations are characteristic of chain reactions. Hence it may be assumed that hydropolymerization of olefins takes place by a chain mechanism, hitherto an infrequent phenomenon in heterogeneous

catalyses. The heterogeneous-catalytic character of this reaction has been demonstrated in particular by experiments with a gas mixture diluted with an inert gas (nitrogen [21]) and also by the effect of adsorption displacement of the olefin (propene, butene) by carbon monoxide on the course of the reaction [22].

TABLE 4

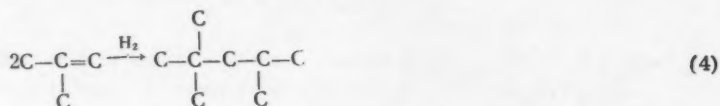
Initial olefin	Yield of hydropolymerization product, % of initial olefin	Increase in yield on addition of 5% CO to initial mixture
Ethylene	0.0	∞ times
Propene	1.9	15-18 *
1-Butene	2.1	10-12 *
1-Hexene	7.6	2-3 *
Isobutene	18.0	3 *

product from a ternary olefin-H₂-CO mixture is many times greater than from a binary olefin-H₂ mixture, and the more so, the lower the molecular weight of the olefin. Apparently, in the absence of CO, surface alkyl radicals formed by semihydrogenation of olefins [reaction (3)] and by hydrogenolysis behave as initiators. The role of the hydrocarbon radicals formed as a result of hydrogenolysis is particularly clearly revealed in the hypopolymerization of isobutene, an olefin which exhibits the greatest tendency towards reaction in the absence of CO (see Table 4).

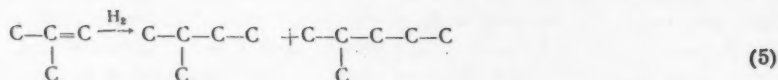
In the absence of CO, isobutene can undergo hydropolymerization in fundamentally different ways depending on the concentration of H₂ in the initial binary mixture [23]. When iso-C₄H₈: H₂ = 3, true polymerization of isobutene predominates with the formation of Butlerov dimers and trimers:

In addition to the active intermediate arising through incomplete reduction of CO, semihydrogenated olefin species — surface alkyl radicals — play a considerable part in the hypopolymerization. Unlike ethylene, its homologs can to a certain extent hypopolymerize in a mixture with H₂, also in the absence of CO.

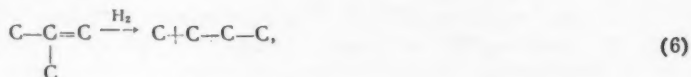
Table 4 gives the yields of the hydropolymerization products from equimolar olefin-hydrogen mixtures and also the factor by which these yields increase when 5% CO is added to the initial binary mixture. It is evident that the yield of the hydropolymerization



When $\text{iso-C}_4\text{H}_8 : \text{H}_2 = 1$, stepwise formation of isobutane homologs, 2-methylalkanes and the corresponding alkenes, take place:

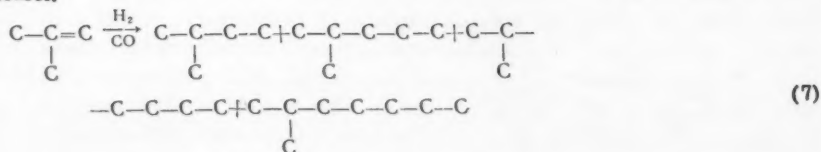


In this reaction, which shall be called "destructive hydropolymerization" of isobutene, isobutene at first undergoes hydrogenolysis to species with one and three carbon atoms,



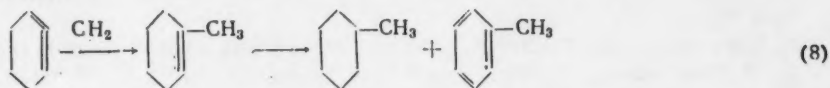
which then interact with undecomposed isobutene molecules, yielding its homologs.

After complete hydrogenation, the hypopolymerization product was found to contain up to 20% of 2-methylbutane and 30% of 2-methylpentane. On addition of 5% CO to an equimolar isobutene - hydrogen mixture, the yield of the hypopolymerization product increased approximately three times (up to 60% of the initial olefin); the nature of the reaction does not change but the yield of hydrocarbons of higher molecular weight of the same type, i.e., of the higher homologs, increases:

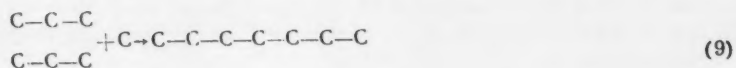


After hydrogenation, the hydropolymerization product contained 6% of 2-methylbutane, 9% of 2-methylpentane, 15% of 2-methylhexane, and 10% of 2-methylheptane.

It is evident from these results that active surface species of the same type are formed in the hydrogenolysis of isobutene and in the incomplete reduction of CO. This was also confirmed by the fixation with cyclohexane of radicals containing one carbon atom formed in the hydrogenolysis of isobutene according to Eq. (6). Cyclohexane added to an equimolar isobutene - hydrogen mixture undergoes conversion into its methyl derivatives to the extent of 15%. The reaction products were found to contain methylcyclohexane and toluene, products of the irreversible catalytic conversion of methylcyclohexene:



An equimolar mixture of isobutene and hydrogen containing 20% CO undergoes conversion, in small yields, into a hydropolymerization product which, after complete hydrogenation, contains up to 33% of n-heptane. The formation of a hydrocarbon with a straight chain containing 7 carbon atoms confirms that isobutene breaks down according to Eq. (6) as follows:



Such a "bridge" scheme was proposed by the present author long before these experimental data were obtained [24]. It should be mentioned that hydrogenolysis in which a surface radical is formed under conditions of hydropolymerization is assumed to involve the conversion of the olefin into a semihydrogenated form which then breaks down into a smaller radical and a lower homolog of the olefin [25].

The behavior of olefins of various structures has been studied in their hydrocondensation reactions with carbon monoxide and also in their hydropolymerization under the influence of CO. Straight-chain olefins enter into these reactions much more readily than branched-chain olefins with the same number of carbon atoms in the molecule, and more readily the lower their molecular weight. α -Olefins are much more reactive than β -olefins of the same molecular weight. The latter isomerize to the α -form before reacting [18, 19].

SUMMARY

1. Catalytic hydrocondensation reactions of CO with olefins and the hydropolymerization of the latter in the presence of H_2 under the influence of small quantities of CO lead to the synthesis of mixtures of aliphatic hydrocarbons, predominantly of straight-chain structure, with a considerable proportion of higher olefins.
2. These reactions take place with the formation of active surface intermediates - products of incomplete reduction of CO and semihydrogenated olefin species - which influence their rates and nature.
3. Carbon monoxide in a mixture with hydrogen behaves, on the one hand, as a methylating agent or an agent responsible for the formation of higher homologs, and on the other, as an initiator of the olefin hydropolymerization.
4. The major role of hydrogenolysis in the formation of active species on the catalyst surface has been demonstrated on the example of a new reaction - destructive hydropolymerization of isobutene.

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BRIEF COMMUNICATIONS

THE EFFECT OF THE NITROGEN FUNCTION OF 4-KETO- DECAHYDROQUINOLINE ON THE RELATIVE STABILITY OF CIS AND TRANS ISOMERS

É. A. Mistryukov and V. F. Kicherov

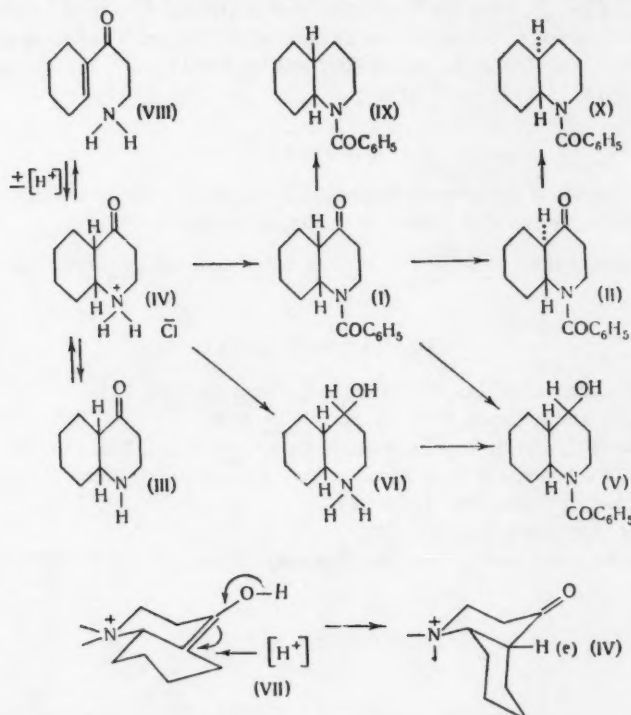
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

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No. 7, pp. 1343-1344, July, 1961

Original article submitted January 7, 1960

In one of our previous communications [1] we described the synthesis of N-benzoyldecahydro-4-quinolone with m. p. 109° (II), which differed from the analogous compound with m. p. 145° (I) obtained earlier [2]. Study of these isomers showed that the benzamide (I) was the primary product of the reaction of benzoylation of decahydro-4-quinolone (III) and could easily be isomerized into benzamide (II). By benzoylation of the base (III) or the hydrochloride (IV) of decahydro-4-quinolone (I) we showed that these substances and the unstable benzamide isomer (I) belonged to the same series of joined rings. The absence of isomerization in going from the base (III) \rightleftharpoons hydrochloride (IV) was also confirmed by catalytic reduction of the ketones (I) and (IV) respectively to N-benzoyldecahydro-4-quinolol (V, m. p. 104°) and the hydrochloride of decahydro-4-quinolol (VI, m. p. 275°), where the amine hydrochloride (VI) on benzoylation gave benzamide (V). Thus it was shown that the stable isomer of N-benzoyldecahydro-4-quinolone (II) and the base (III) or the hydrochloride (IV) of decahydro-4-quinolone belong to different series in the linking of the rings. In distinction from N-benzoyldecahydro-4-quinolone, for which we obtained both isomers (I) and (II), extreme instability of one of the isomers is characteristic for decahydro-4-quinolone hydrochloride.



In the cation of hydrogen chloride on base (III) or in the saponification of benzamide (II) by boiling with hydrochloric acid, there is formed only one hydrochloride (IV). This fact can be explained by the effect of ammonization

of the nitrogen in the process of ketonization of the cation of enol (VII), common to the *cis* and *trans* forms. Due to the strong electrostatic repulsion, cation (VII) orients the entering at $C_{(10)}$ proton in the direction most removed from the bond $\overset{+}{N}-C_{(9)}$, and on ketonization there is produced ketone (IV) with equatorial hydrogen on $C_{(10)}$, that is, the *cis* isomer. Also, in the base the lability of the bond $\overset{+}{N}-C$ in β -amino acids [3] and 4-piperidones [4] suggests that for shift of the equilibrium (IV) \rightleftharpoons (VIII) toward formation of the cyclic ketone (IV) requires a coplanar bond $C_{(9)}-N$ and $C_{(10)}-N$, and this also permits the assumption of formation of the *cis* isomer of the aminoketone. Ketone (IV) can be considered as a reaction which reverses the Hofmann degradation of ammonium bases (cf. [5]).

In the reduction of benzamides (I) and (II) by desulfurization of the corresponding thioketals we obtained N-benzoyldecahydroquinolines with m. p. 57° (IX) and 97° (X), the configurations of which were determined earlier [6] as respectively *trans* and *cis* on the basis of the Auwers-Skita rule. If this stereochemical determination is used [6], it becomes difficult to understand the fact of easy isomerization of benzamide (I) in which the chief properties of the amino group are neutralized by benzoylation into benzamide (II). Evidently the above determination must be reversed and it must be considered that benzamide (IX) is the *cis* isomer and benzamide (X) the *trans* isomer of N-benzoyldecahydroquinoline. This suggestion is also confirmed by the results of the reduction of derivatives of 4-ketodecahydroquinoline. In the hydrogenation of (IV) in water solution or of (I) in dry dioxane there are formed chiefly (about 90%) the corresponding alcohols (VI) and (V). Study of the infrared spectrum of benzamide (V) in chloroform solution shows the presence of two absorption bands in the region of the bond C—O (1050 and 1034 cm^{-1}), which evidently correspond to the presence in this solution of a mixture of two conformational types with equatorial and axial positions of the hydroxyl [7]. The other isomeric N-benzoyldecahydro-4-quinolol of this series (m. p. 140°) has one absorption band at 1025 cm^{-1} , which corresponds to the axial position of the hydroxyl group. In the reduction of ketone (III) by sodium in alcohol, chiefly (about 80%) there is formed the isomer of the alcohol which corresponds to hydrochloride (VI) or benzamide (V). This result, and also the double absorption of bond C—O in benzamide (V) agree with the above suggestion that this ketone (III) is *cis*-decahydro-4-quinolone, since only in this case is it possible to have conversion of the hydroxyl group from the axial to the equatorial position and the reverse. In catalytic reduction or reduction by aluminum isopropylate of ketone (II) we obtained the isomer of N-benzoyldecahydro-4-quinolol (XI, m. p. 222°), which had the axial position of the hydroxyl group (ν_{max} 1041 cm^{-1}). The other isomer of the *trans* series (m. p. 139°, ν_{max} 1052 cm^{-1}) was obtained in yield of 53% from a mixture formed in reduction of (II) by NaBH_4 in aqueous methanol. All the above alcohols of the *cis* series and N-benzoyl-*cis*-decahydroquinolines also had characteristic absorption in the region 1027 and 1018–1017 cm^{-1} ; the analogous compounds of the *trans* series had them in the region 1010–1005 cm^{-1} (cf. [5]).

SUMMARY

1. The most stable isomers of the bases or hydrochlorides of decahydro-4-quinolone and N-benzoyldecahydro-4-quinolone belong to different groups with respect to linking of the rings.
2. We suggest the need to review the stereochemical determinations of Hückel for the *cis* and *trans* decahydroquinolines.

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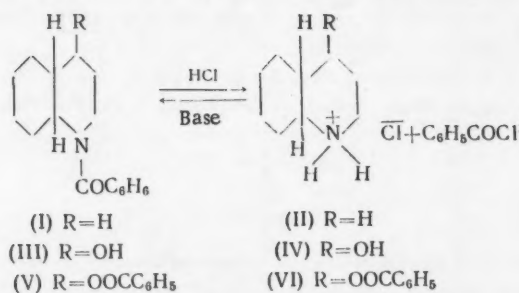
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THE REVERSE SCHOTTEN-BAUMAN REACTION AND THE
STEREOCHEMISTRY OF DECAHYDROQUINOLINE AND
ITS DERIVATIVES*

É. A. Mistryukov and V. F. Kicherov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR
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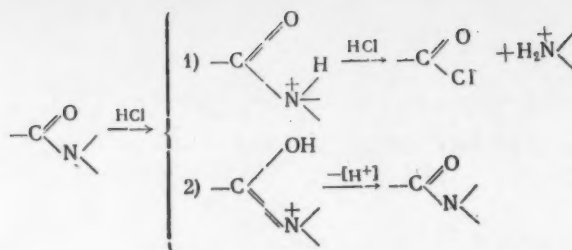
One of the widely used methods of obtaining O-esters of amino alcohols and establishing the spacial structures of these compounds is the method of N → O acyl rearrangement. Here it is assumed that this reaction occurs intramolecularly [1] through intermediate formation of a cyclic intermediate product of a ketal type [2]. In the present communication we have described one possible path of N → O migration under the action of a solution of hydrogen chloride in dioxane. We have shown that some benzamino alcohols under these conditions can be split to benzoyl chloride and amine hydrochlorides with later intermolecular esterification on the hydroxyl. The reaction of hydrogen chloride with benzamides is a stereospecific reaction which depends greatly on the spacial structure of the amide. Thus, N-benzoyl-cis- and trans-decahydroquinolines differ sharply in the character of the reaction with dry hydrogen chloride; on short boiling with dioxane solutions of hydrogen chloride of N-benzoyl-cis-decahydroquinoline (I)



the latter is quickly split into benzoyl chloride and cis-decahydroquinoline hydrochloride (II) with a yield of more than 75%. Under analogous conditions N-benzoyl-trans-decahydroquinoline is not changed. This stereospecific splitting of the benzamides was used to show structures and for obtaining some derivatives of (I). Thus both isomeric N-benzoyl-cis-decahydroquinolols (III) (m. p. 104° and 140°) were smoothly split to hydrochlorides (IV) (m. p. 275 and 230° respectively) with yields of about 80%. The analogous alcohols of the trans series [3] under these conditions were not changed. The above method permits selective removal of the N-benzoyl group in O,N-dibenzoyl derivatives of cis-decahydro-4-quinolols (V) and thus selective obtaining of the hydrochlorides of the O-esters (VI).

For the synthesis of 4-benzoyloxydecahydroquinoline hydrochloride (m. p. 278°) this path of synthesis is the only acceptable one, since decahydro-4-quinolol hydrochloride with m. p. 275° does not react under mild conditions with benzoyl chloride (cf. [4]), and under more severe conditions forms exclusively the O,N-dibenzoate. Obtaining the hydrochloride of the O-ester by N → O rearrangement of the amide is also impossible, since none of the four previously obtained [3] isomeric N-benzoyldecahydroquinolols rearranges into the corresponding O-ester (cf. [4, 5]). The role of spacial factors in determining the different character of the reactions of the isomeric benzamides with anhydrous hydrogen chloride evidently leads to protonization of the amide [6]. In the case of splitting of the amide protonization occurs on the nitrogen (path 1) or on the oxygen of the benzoyl group (path 2) for the unsplit amide

* For the configuration of isomers of decahydroquinolines and decahydro-4-quinolols see [3].



As a model compound with a structure analogous to the structure of the heterocyclic part of N-benzoyl-trans-decahydroquinoline we studied the action of hydrogen chloride on N-benzoylpiperidine. This compound was almost unchanged (yield of piperidine hydrochloride less than 10%) under the conditions described, which also confirms the above [6] suggestion of the structure of the decahydroquinolines.

SUMMARY

1. We have suggested a new method for splitting benzamides, based on the action of dry HCl in dioxane, and have shown the stereospecificity of this reaction.

2. We have suggested a new method for the synthesis of O-esters of some amino alcohols which cannot be obtained by N → O acyl migration.

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THE SYNTHESIS OF N-TRIALKYLBORAZINES FROM ALKYLAMINE-BORANES IN THE PRESENCE OF MERCAPTANS

B. M. Mikhailov and V. A. Dorokhov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

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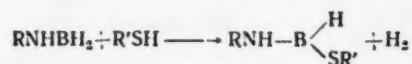
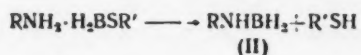
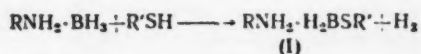
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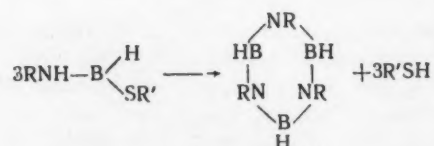
In studying the action of mercaptans on diethylamine-borane, we obtained monomers which distilled without decomposition and symmetrization of alkylmercapto-(diethylamino)boranes [1]. Starting from different dialkylamine-boranes, we synthesized a series of other alkylmercapto-(dialkylamino)boranes which had interesting chemical properties. In this connection we were interested in studying the behavior of complexes of boranes and primary amines with respect to mercaptans. Here we would expect formation of alkylmercapto-(alkylamino)boranes, which, as follows from experiments on the action of primary amines on tetraalkylmercaptodiboranes, are unstable [2] and are easily converted into N-trialkylborazines with splitting of the mercaptan [2].

As our experiments showed, addition to ethylamine-borane of an equimolecular amount of n-butyl mercaptan caused considerable evolution of hydrogen even at room temperature. With gradual heating to 80° in the course of five hr, the theoretical amount of hydrogen was evolved (2 M per 1 M ethylamine-borane), and on distillation N-triethylborazine was obtained with a yield of 85%. Other alkylamineboranes behaved in the same way toward mercaptans. In the first stage of the process it is evidently analogous to the reaction of mercaptans with diethylamine-borane [1].

At first, when mercaptans act on alkylamine-boranes a complex of alkylmercaptoborane with the amine (I) is formed with evolution of hydrogen, and this splits out the mercaptan, being converted to alkylaminoborane (II). In its turn (II) reacts with mercaptan forming alkylmercapto-(alkylamino)borane (III)



Then (III), splitting out mercaptan, is condensed into N-tri-alkylborazine (IV)



Since in this process the mercaptan is constantly regenerated, the synthesis of N-trialkylborazines from alkylamine-boranes can be carried out using small amounts of mercaptan, which plays the part of the catalyst for the reaction. Thus, we obtained N-triethyl-, N-triisobutyl-, and N-tri-n-butylborazines with yields of 75-87% by heating the corresponding alkylamine-boranes with small addition of mercaptan at 80-100°. Somewhat higher temperatures (to 130°) are needed for transformation of methylamine-borane into N-trimethylborazine.

When alkylamine-borazines are heated to 120° without mercaptan, evolution of hydrogen occurs in a quantity about equivalent to the formation of alkylaminoboranes. When mercaptan is later added to the reaction mixture at the same temperature, the formation of N-trialkylborazines goes to conclusion.

The transformation of alkylamine-boranes into N-trialkylborazines was previously studied by various authors [3-6]. This reaction in all their work was carried out with a high vacuum technique and required high temperatures (200-300°). Our catalytic method permits preparation of N-trialkylborazines in large amounts at moderate temperatures, using the ordinary apparatus of organic synthesis. The starting alkylamine-boranes can be obtained either by passing diborane into an ether solution of alkylamine, or by reaction of an amine salt with lithium borohydride in ether solution [6, 7].

EXPERIMENTAL

All the operations were carried out in an atmosphere of dry nitrogen. Methylamine-borane and ethylamine-borane were prepared with almost quantitative yield by passing a small excess of diborane into an ether solution of amine at -30° and later distillation of the ether in a vacuum. The thus obtained alkylamine-boranes were used without further purification.

N. Trimethylborazine. In a flask with a reflux condenser, connected to a gasometer, were placed 6.1 g (0.136 M) of methylamine-borane and 1 ml of n-propyl mercaptan; the flask was heated on an oil bath for eight hr and the temperature was gradually raised to 130°. On distillation we obtained 4.5 g (80%) of N-trimethylborazine with b. p. 131-133°, n_D^{20} 1.4375. The literature gives [6] b. p. 133°, n_D^{20} 1.4404. In the experiment we obtained 0.27 M of hydrogen (under normal conditions).

N-Triethylborazine. To 8.5 g (0.144 M) of ethylamine-borane was added 1 ml of butyl mercaptan. The mixture was heated quite rapidly to 60° and then slowly to 100° in the course of five hr; on this, 0.29 M of hydrogen was evolved. On distillation of the reaction product we obtained 6.9 g (87%) of N-triethylborazine with b. p. 72-74° (25 mm), n_D^{20} 1.4380; the literature gives b. p. 66-68° (20 mm), n_D^{20} 1.4380 [2].

N-Trisobutylborazine. In a solution of 10.3 g (0.141 M) of isobutylamine and 50 ml of ether was passed 0.16 M of diborane at 5-10°. The solvent was distilled off and the residue was treated with 1 ml of butyl mercaptan; the mixture was heated at 80-100° for two hr, during which 0.28 M of hydrogen was evolved. On distillation we obtained 10.1 g of N-trisobutylborazine with b. p. 92-94° (3 mm), D_4^{20} 0.8245, n_D^{20} 1.4466. Yield, calculated on the starting amine 86%. Found: C 57.91; H 12.25; B 12.68%. $C_{12}H_{30}N_3B_3$. Calculated: C 57.91; H 12.15; B 13.04%.

N-Tri-n-butylborazine. In an analogous manner to the preceding experiment, from 6.8 g (0.093 M) of n-butylamine with addition of 0.8 ml of butyl mercaptan we obtained 5.8 g of tri-n-butylborazine with b. p. 109-111° (3.5 mm), n_D^{20} 1.4524. The literature gives [2] b. p. 78-80° (0.25 mm), n_D^{20} 1.4515. The yield of borazine was 75% calculated on the amine used in the reaction. In the experiment we obtained 0.19 M of hydrogen.

SUMMARY

We have suggested a simple method for preparing N-trialkylborazines from alkylamine-boranes in the presence of small amounts of mercaptans, which play the role of catalysts for the reaction.

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THE SYNTHESIS OF SOME MOMOKETONES OF THE CIS-HYDRINDANE SERIES

V. F. Kucherov, L. N. Ivanova, and T. A. Severina

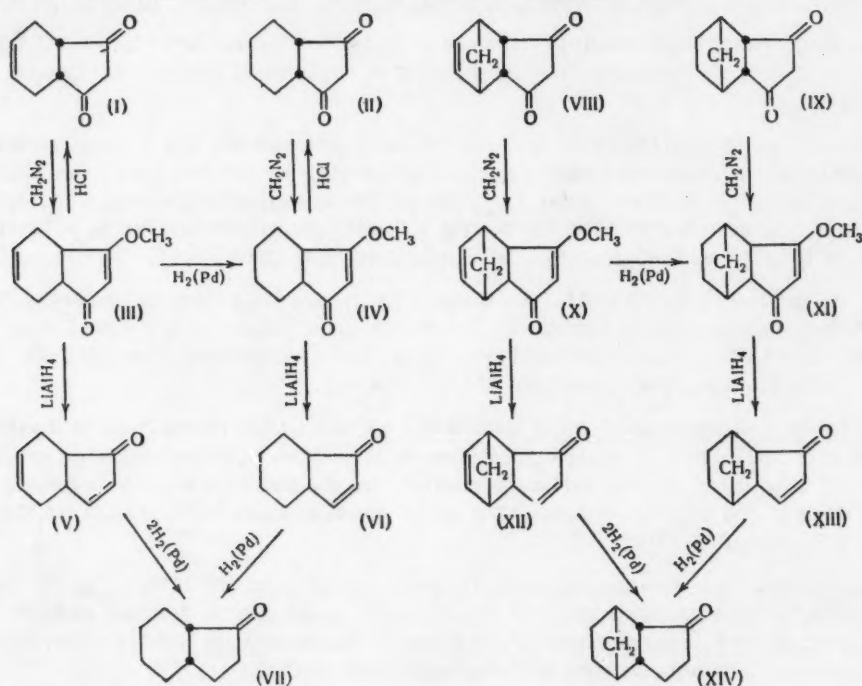
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

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As was shown previously [1,2], the use in the diene condensation of such dienophils as cyclopenten-1,3-dione permits easy preparation of polycyclic β -diketones related to steroid compounds. In order to use such β -diketones for the synthesis of polycyclic monoketones with ketone groups on the five membered ring, we studied the frequently used simplest β -dicarbonyl cyclic compounds [3] by reduction of the enol ethers of these β -diketones with lithium aluminum hydride. The *cis*- adduct (I) and the corresponding *cis*-hydrindan-1,3-dione (II) by treatment with diazomethane easily gave the corresponding methyl ethers of the enols (III) and (IV), by reduction of which with lithium aluminum hydride we obtained good yields of unsaturated monoketones (V) and (VI). On hydrogenation of the latter with a Pd catalyst there was absorbed respectively one or two moles of hydrogen and we obtained quantitatively *cis*- α -hydrindanone (VII). An analogous transformation was also carried out for the adduct (VIII) and endomethylene-*cis*-hydrindan-1,3-dione (IX) which gave good yields of the previously little accessible monoketones (XII), (XIII), and (XIV), which by the methods of their synthesis had an *endo-cis*-configuration.



These results show the possibility of using polycyclic β -diketones for stereospecific synthesis of compounds related to the steroids which are the subject of our further investigation.

EXPERIMENTAL

Obtaining methyl ethers of the enols. To a suspension of 1 g of adduct (I) in 7 ml of ether was added an ether solution of diazomethane to solution, and the mixture remained overnight at 0°. On distillation we obtained 0.85 g of methyl ether (III): b. p. 105-105.5° (0.5 mm), n_D^{20} 1.5331; m. p. 40-41° (from ligroin), λ_{\max} 240 m μ (alcohol), ϵ 9800. Found: C 73.16, 73.14; H 7.15, 6.95%. $C_{10}H_{12}O_2$. Calculated: C 73.14; H 7.37%. On saponification of (III) with dilute hydrochloric acid at room temperature we obtained the starting diketone (I) quantitatively.

In an analogous way from 1.7 g of (II) we obtained 1.65 g of methyl ether (IV) which after two distillations had b. p. 102-103° (1 mm), n_D^{21} 1.5212; λ_{\max} 230 m μ (isooctane), ϵ 11100. Found: C 72.12, 72.22; H 8.18, 8.35%. $C_{10}H_{14}O_2$. Calculated: C 72.26; H 8.49%. The same enol ether could be obtained in quantitative yield from hydrogenation of (III) with a Pd catalyst in methanol.

On treatment with diazomethane, 3.24 g of adduct (VIII) gave 2.5 g of the corresponding methyl ether (X), m. p. 73-74° (from ligroin); λ_{\max} 245 m μ (alcohol), ϵ 11100; Found: C 75.12, 74.91; H 6.75, 6.77%. $C_{11}H_{12}O_2$. Calculated: C 74.97; H 6.86%.

Analogously from 0.82 g of (IX) we obtained 0.8 g of methyl ether (XI) with b. p. 118-118.5° (0.5 mm), n_D^{20} 1.5380; λ_{\max} 243 m μ (alcohol), ϵ 12400. Found: C 73.82, 74.04; H 7.89, 7.87%. $C_{11}H_{14}O_2$. Calculated: C 74.13; H 7.92%. The same ether was formed on catalytic hydrogenation of (X) in methanol solution with Pd/CaCO₃.

Reduction of the methyl ethers of the enols with lithium aluminum hydride. To a solution of 246 g of (III) in 150 ml of absolute ether we slowly added 15 ml of 1 M ether solution of lithium aluminum hydride and stirred in boiling ether for 2.5 hr. On the next day the excess LiAlH₄ was decomposed with moist ether (50 ml) and water (25 ml) and 80 ml of dilute hydrochloric acid (1:1) was added; the mixture was stirred for 4 hr at room temperature. The ether layer was separated, the water layer was extracted with ether, and the combined ether extracts were washed with a small amount of water and dried with magnesium sulfate. After distillation of the ether and two distillations we obtained 1.2 g (yield 60%) of unsaturated ketone (V), b. p. 70-71.5° (1.5 mm), n_D^{23} 1.5218; λ_{\max} 216 m μ (isooctane), ϵ 6300. Found: C 80.25, 80.30; H 7.70, 7.70%. $C_9H_{10}O$. Calculated: C 80.56; H 7.51%.

In an analogous way from 3.5 g of (IV) we obtained 2.1 g (yield 70%) of unsaturated ketone (VI), b. p. 55-57° (1 mm), n_D^{15} 1.5070; λ_{\max} 218 m μ (isooctane), ϵ 3500. Found: C 79.05, 79.06; H 8.66, 8.88%. $C_9H_{12}O$. Calculated: C 79.37; H 8.88%.

On reduction of 1.76 g of (X) we obtained 1.4 g of a dark oil which was kept in a vacuum in a stream of nitrogen, dissolved in benzene, and passed through a column with Al₂O₃. We obtained 0.9 g (yield 62%) of unsaturated ketone (XII), m. p. 62-63° [4] (from ligroin); λ_{\max} 221 m μ (isooctane), ϵ 6850. Found: C 82.37, 82.40; H 6.96, 6.78%. $C_{10}H_{10}O$. Calculated: C 82.16; H 6.90%. The 2,4-dinitrophenylhydrazone had m. p. 188-189.5°. Found: C 58.66, 58.47; H 4.40, 4.44%. $C_{16}H_{14}O_4N_4$. Calculated: C 58.89; H 4.32%.

In an analogous way from 5.3 g of (XI) we obtained 3.3 g (yield 75%) of unsaturated ketone (XIII) with m. p. 50-51° (from ligroin); λ_{\max} 222 m μ (isooctane), ϵ 9400. Found: C 80.78, 81.12; H 8.30, 8.08%. $C_{10}H_{12}O$. Calculated: C 81.04; H 8.16%. The 2,4-dinitrophenylhydrazone had m. p. 178-180° (from alcohol). Found: C 58.51, 58.60; H 5.01, 4.98%. $C_{16}H_{16}O_4N_4$. Calculated: C 58.53; H 4.91%.

Obtaining cis- α -hydrindanone (VII). A solution of 1.5 g (0.011 M) of (VI) in 20 ml of absolute methanol was hydrogenated over a Pd catalyst. After absorption of one mole of hydrogen, hydrogenation was stopped, the solvent was distilled off in a vacuum, and the residue was distilled. We obtained 1.2 g of cis- α -hydrindanone (VII) with b. p. 57-58° (1 mm), n_D^{20} 1.4830; ν (alcohol) 1739 cm⁻¹. Found: C 78.38, 78.22; H 10.24, 10.22%. $C_9H_{14}O$. Calculated: C 78.21; H 10.21%.

The 2,4-dinitrophenylhydrazone obtained in the usual way had m. p. 126-127°; λ_{\max} 365 m μ (alcohol); semicarbazone m. p. 210-211°, and oxime m. p. 77-80°, which agreed with the literature data [5]. In an analogous way we hydrogenated the unsaturated ketone (V). Two moles of hydrogen were absorbed and hydrogenation was stopped. We obtained a quantitative yield of cis- α -hydrindanone (VII).

Obtaining endomethylene-cis- α -hydrindanone (XIV). A solution of 0.82 g (0.0056 M) of (XII) in 10 ml of absolute methanol was hydrogenated over a Pd catalyst. After absorption of two moles of hydrogen, hydrogenation was stopped, the solvent was distilled off, and the residue (0.77 g) was sublimed in a vacuum (3 mm) to give (XIV), m. p. 96-97°; ν (alcohol) 1735 cm⁻¹. Found: C 79.69, 79.93; H 9.52, 9.39%. $C_{10}H_{14}O$. Calculated: C 79.95; H 9.39%. The 2,4-dinitrophenylhydrazone had m. p. 157-158° (from alcohol); λ_{\max} 365 m μ (alcohol). Found: C 58.21, 58.37; H 5.48, 5.45; N 17.10, 16.98%. $C_{16}H_{18}O_4N_4$. Calculated: C 58.1; H 5.49; N 16.96%.

Analogous hydrogenation of the unsaturated ketone (XIII) was carried out. One mole of hydrogen was absorbed, and hydrogenation was stopped. We obtained a quantitative yield of (XIV).

SUMMARY

We have worked out a path for the synthesis of some monoketones of the cis-hydrindane series.

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A RAPID, SIMPLE METHOD FOR MICRODETERMINATION OF CARBON AND HYDROGEN IN MONOMERS AND POLYMERS OF FLUORO-ORGANIC COMPOUNDS

A. I. Lebedeva, N. A. Nikolaeva, and V. A. Orestova

Institute of High Molecular Compounds, Academy of Sciences of the USSR

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Many of the methods known at present for determination of carbon and hydrogen in organic fluorine compounds cannot pretend to simplicity of rapidity in performance. In a number of methods a complicated multilayer filling of the tube is used [1-4]. In the case of perfluoro- or highly fluorinated compounds it is often necessary to add water [5] or benzoic acid [1, 6]. The lead preparations used as a filler, in pure form or deposited on pumice [7-9], react with platinum and quartz. Also, with use of PbO_2 there is less assurance of correctness of the results for hydrogen. In simultaneous determination of several elements additional apparatus is needed for pyrohydrolysis of magnesium fluoride [10] or a number of additional absorbers [11] and the introduction of definite corrections for carbon, hydrogen, and fluorine are required, so that the time of analysis is greatly increased.

TABLE 1.

Substance analyzed	C, %			H, %		
	found	calculated	difference	found	calculated	difference
Benzotrifluoride	57.61	57.53	+ 0.08	3.57	3.42	+ 0.15
$C_7H_5F_3$, 36.01%F	57.57		- 0.06	3.38		- 0.04
Fluoroacetamide	31.16	31.17	- 0.01	5.25	5.22	+ 0.03
C_2H_4ONF 24.66%F	31.23		+ 0.06	5.17		- 0.05
m-Trifluoromethyl-phenylmethacrylamide	57.64	57.64	+ 0.00	4.53	4.37	- 0.16
$C_{11}H_{10}ONF_3$ 24.89%F	57.80		+ 0.16	4.64		+ 0.27
2,4-Dinitrophenylhydrazine of 1,1,1-trifluoroacetone	36.83	36.99	- 0.16	2.49	2.42	+ 0.07
	36.69		- 0.30	2.69		+ 0.27
$C_9H_7O_4N_4F_3$ 19.52%F	8.35	8.62	- 0.27	0.21	0	+ 0.21
1,1,2-Trifluoro-2-chloro-1,2-dibromoethane			- 0.02	0.22		+ 0.22
$C_2ClBr_2F_3$ 20.63%F	8.60	43.24	- 0.11	2.50	2.27	+ 0.23
Thenoyltrifluoroacetone	43.13		+ 0.07	2.38		+ 0.11
$C_8H_5O_2SF_3$ 25.65%F	43.31	25.86	+ 0.01	6.50	6.50	+ 0.00
Difluorodimethylborazine	25.87		+ 0.00	6.64		+ 0.14
$BF_2N(CH_3)_2$ 49.94%F	25.86					

EXPERIMENTAL

In this work we have investigated the possibility of using silver metavanadate ($AgVO_3$) deposited on pumice for microdetermination of carbon and hydrogen in organic fluorine monomers and polymers. Silver vanadate on pumice was previously used for analysis of organic [12] and tin organic compounds [13], where it was shown that it was completely indifferent to CO_2 [14]. Although in effectiveness silver vanadate yields to a whole series of

catalysts of similar type [15, 16], yet in the determination of carbon and hydrogen in organic fluorine monomers and polymers with silver metavanadate we have obtained good results (Tables 1, 2).

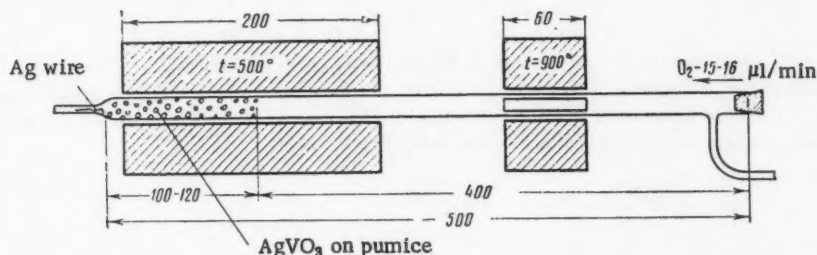
The mechanism of action of silver vanadate is still not perfectly clear. Probably the combination of silver and vanadium pentoxide on the pumice is a good oxidizing reagent and at the same time a valuable absorbent for combustion products which contain fluorine.

TABLE 2

Substance analyzed	Found with MgO [10]			Found with AgVO ₃ on pumice		
	sample, mg	C, %	H, %	sample, mg	C, %	H, %
Polytetrafluoroethylene (-C ₂ F ₄) _n , 75.98%		24.02*	—	3,920	24.24	0.25
Polymer 1**	4,040	74.10	5.87	5,265	24.10	0.33
				3,270	74.36	5.83
Polymer 2	5,430	74.43	6.07	3,805	74.52	5.94
	3,640	72.53	5.41	3,000	72.22	5.50
Polymer 3	3,510	72.27	5.64	3,460	72.09	5.66
	3,605	75.69	6.13	4,350	75.69	6.11
Polymer 4	3,250	75.24	5.95	4,800	75.56	6.06
	2,390	64.57	4.71	3,755	64.57	4.62
	3,100	64.75	4.60	3,650	64.38	4.44

*Carbon content calculated theoretically.

** The polymers were synthesized in the Institute of High Molecular Compounds, Academy of Sciences, USSR; determination of carbon and hydrogen was carried out for comparison by two processes.



Tube with filling for analysis of organic fluorine compounds.

The catalyst was prepared by fusing in a quartz crucible 8 g of already treated pumice [17] with grain size 1-2 mm, and 5 g of pure commercial AgVO₃ for 1.5-2 hr at 400° with stirring and later ignition in a muffle at 800° for 4 hr. In a quartz combustion tube (figure) we placed a layer (10-12 cm) of ignited AgVO₃ on pumice. In the outlet of the tube we placed a piece of silver wire. The tube was heated in a stream of oxygen for 30 min. A sample of 3-6 mg of the fluorine-containing compound was placed in the tube in a quartz or platinum boat and burned with the aid of an electric heater in a stream of oxygen at a rate of 15-16 ml/min for 15-17 min. The total amount of oxygen was 250 ml. The temperature of the large oven was 500°, of the electric heater 900°. Carbon and hydrogen were determined as usual by weight of CO₂ and H₂O without introducing any corrections.

The time required for the complete analysis was 40-45 min. Fluorine was determined separately in a flask filled with oxygen [18].

SUMMARY

1. We have suggested a simple and convenient method for microdetermination of carbon and hydrogen in organic fluorine compounds. The determination is carried out by burning the sample of substance in a stream of oxygen in a quartz tube with a filler of silver metavanadate on pumice.

2. The method is useful for monomers and polymers of fluorine and perfluoroorganic compounds with fluorine content up to 75%. Chlorine, bromine, nitrogen, sulfur, and boron do not change the determination. The error of the method is $\pm 0.3\%$.

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THE ELECTROCHEMICAL BEHAVIOR OF PYRIDINE

G. A. Tedoradze, S. G. Maïranovskii, and L. D. Klyukina

Institute of Electrochemistry, Academy of Sciences of the USSR and

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

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In an attempt to study the catalytic wave caused by pyridine on a rotating amalgamated disk electrode we encountered a number of unexpected effects. We chiefly noted that in distinction from a mercury dropping electrode the polarization curve on the disk electrode in a borax solution (within the observed rate of rotation of the electrode of 100-6000 rpm and concentration of pyridine 10^{-3} to 10^{-2} m/liter) did not have a bend down to the potential of liberation of sodium. On the curve we found only a continuous increase in current with a rise in potential. On repeatedly obtaining the curve with the same electrode and in the same solution the polarization curve each time lay markedly above the preceding one. Reproducible results could be obtained only by changing the solution and again amalgamating the electrode. It should be noted that when the electrode potential was unchanged the current continuously increased with time of electrolysis.

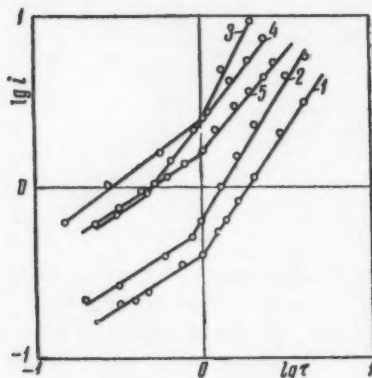
On obtaining the polarization curve on a suspended mercury drop in a solution of 2 N $\text{Li}_2\text{B}_4\text{O}_7$ in the presence of 0.94 M of pyridine we found that beginning with a potential 1.64-1.66 v (dropping electrode), the drop was covered with a continuous film of product which did not conduct the current. More detailed investigation showed that in the buffer solution of pyridine, along with the catalytic evolution of hydrogen there was evidently formation of a product from reduction of pyridine; one which had a high surface activity and great catalytic activity (compared to pyridine). We noted the formation of this product especially in concentrated pyridine solutions. At concentrations of the latter above 0.5 M the evolution of hydrogen in general did not occur; all the current went to the formation of this apparently polymerized product, which was almost insoluble in water. The formation of the polymeric product evidently also caused the observed increase in current with time on the rotating disk electrode. The increase in current with lengthening of the period of the dropping electrode was observed by Kuta and Drabek [1] in polarography of a solution of pyridine. This increased current was interpreted as the appearance of a surface wave because of adsorption of pyridine [2].

EXPERIMENTAL

In order to test whether such an increase in current was due to adsorption of pyridine on the mercury dropping electrode or the result of adsorption of the product of pyridine reduction, we determined the curve of current strength-time with a capillary which had a movable opening (moved by a microcrew) and which permitted a change over a wide range of time of dropping with practically unchanged rate of outflow of mercury "m." Part of the i - t curve was taken on an oscillograph. When reproducible results were obtained, the solution under study in the cell was changed after each 3-4 measurements, the capillary was periodically washed on the outside with nitric acid; polarization of the solution did not exceed 1.9 v. Experiment showed that in the concentration range of 10^{-4} to 10^{-3} M/liter of pyridine, on increasing the period of dropping from 0.2 to 1 sec, the current rose proportionally to $t^{2/3}$. On further increase in the period of dropping from 1 to 4 sec the current rose proportionally $\approx t^{3/2}$ (Fig. 1). Analogously, on the i - t curve taken on the oscillograph during the life of one drop there was also noted a strong increase in current with increasing t ; here the rise in current depending on time did not obey the $t^{2/3}$ law. Increase in current at $\tau > 1$ sec could not be explained by adsorption of pyridine on the mercury dropping electrode, since in this case the current would increase by the $t^{7/6}$ law [3-5]. The absence of any marked "surface" current in catalysis by pyridine is also indicated by the very small adsorbability of pyridine at these potentials.

Calculation of the filling of the surface by the electrocapillary curve [6] with account of the relation of adsorption to potential [7] for $c_{\text{pyr}} = 1$ mM/liter and $\phi = -1.8$ v (dropping electrode) gives a value about $10^{-6}\%$, or, if we assume that the rate constant of the surface catalytic process is close to the order of magnitude of the rate

constant of the volume process, then for the surface catalytic current produced by pyridine under these conditions we would obtain a value of the order of 10^{-4} μ a, that is, a value which could be neglected compared to the volume current (4 μ a), [8]. On the basis of this, we can conclude that in this case the increase in current is not due to adsorption of pyridine, but is due to the accumulation on the electrode surface of the catalytically active product of reduction and polymerization of pyridine. Adsorption of this polymeric product evidently follows the S-shaped isotherm of Frumkin [7], as is indicated by the sharp break in the $\log i - \log t$ curve. It should be noted that formation of the reduction product of pyridine occurs in buffer solutions of different compositions; this indicates that the composition of the buffer evidently does not affect the formation of the polymer. It is true that an analogous effect, in lesser degree, is evidently due to steric factors and is found also in the case of the catalytic wave produced by the homologs of pyridine: β -picoline and 2,6-lutidine.



Relation of average (during life of drop) current to period of dropping at $m = \text{constant}$ in a buffered solution of pyridine, β -picoline, and 2,6-lutidine: 1) 0.27 mM/liter pyridine in 0.1 N solution of borax; 2) 0.137 mM/liter of pyridine in borate buffer, pH 8; 3) 1.16 mM/liter pyridine in ammonia buffer, pH 9; 4) 0.69 M/liter β -picoline in 0.1 N solution of borax; 5) 0.652 mM/liter, 2,6-lutidine in 0.1 N solution of borax.

These results show that to obtain a pure catalytic current for pyridine we must work with solutions not contaminated by polymer from previous experiments, and with well washed dropping electrodes. In order to avoid accumulation of polymer during the life of the drop we must work with capillaries which have a small dropping period (not above 0.5 sec).

SUMMARY

1. In the reduction of pyridine on a mercury dropping electrode, along with the catalytically evolved hydrogen there occurs reduction of pyridine with formation of a surface active polymeric product.
2. The increase in catalytic wave in pyridine solutions with time depends on the catalytic action of the polymeric product which accumulates on the surface.

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LETTERS TO THE EDITOR

THE SYNTHESIS OF BENZONITRILE DERIVATIVES OF ALLYL PALLADIUM CHLORIDE

N. M. Klimenko, I. I. Moiseev, and Ya. K. Syrkin

M. V. Lomonosov Institute of Fine Chemical Technology

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Previously [1] we obtained a complex substance with the composition C_3H_5PdCl (I) by the reaction of $PdCl_2$ and allyl alcohol in aqueous acid solution. A complex of the same composition was obtained by Smidt and Hafner [2] by the action of $PdCl_2$ on pure allyl alcohol, and also by Hüttel and co-workers by the action of allyl chloride with $PdCl_2$ in 50% aqueous acetic acid [3].

It seemed interesting to attempt to synthesize complex (I) by an exchange reaction of $PdCl_2$ with an organic compound of an element in which the element was bound to the allyl radical by a simple σ -bond. For this we chose allyl magnesium chloride.

By addition of palladium chloride to an ether solution of C_3H_5MgCl no visible change occurred in the course of a day. On mixing 15 ml of 0.27 M solution of C_3H_5MgCl in ether, prepared by the method of Gilman [4], and 100 ml of 0.026 M solution of $(C_6H_5CN)_2PdCl_2$ in benzene, there was formation of a bright yellow substance with the composition $C_3H_5PdCl(C_6H_5CN)$. Found: C 41.18; H 4.24; N 4.55; Pd 35.5; Cl 12.15%. $C_{10}H_{10}PdCl$. Calculated: C 41.95; H 3.52; N 4.89; Pd 37.26; Cl 12.38%.

This compound was soluble in benzene, alcohol, tetrahydrofuran, and chloroform, poorly so in ether, insoluble in ligroin. When heated it began to decompose without melting at 115-135° and blackened at 170°. It was stable in air.

We suggest that this compound, like complex (I), represents a new class of complexes, in which the palladium atom reacts with the whole allyl group as a structural unit.

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SILICON ANALOGS OF CARBENES AND THE SYNTHESIS OF THREE MEMBERED HETEROCYCLES WHICH CONTAIN SILICON

M. E. Vol'pin, Yu. D. Koreshkov, and D. N. Kursanov

Institute for Organic Compounds of the Elements, Academy of Sciences of the USSR

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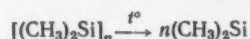
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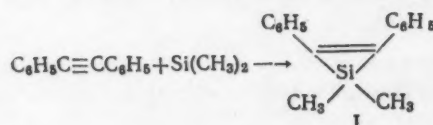
Starting from the similarity in electron structure of derivatives of divalent carbon (carbenes) and divalent silicon, we can expect similar reactivities in these compounds. For obtaining alkyl derivatives of divalent silicon we have studied the reaction of dimethyldichlorosilane with sodium in boiling xylene:



and the thermal splitting of Si-Si bonds in the polymer $[(\text{CH}_3)_2\text{Si}]_n$ (where $n \approx 55$ [1]).



We hoped that in carrying out these reactions in the presence of toluene there would be formed the intermediate $(\text{CH}_3)_2\text{Si}$ which would combine with a triple C≡C bond to form a three membered heterocycle (I) by the mechanism



Actually in both cases from the reaction products we isolated the same stable product of addition of $\text{Si}(\text{CH}_3)_2$ to toluene, with the composition $\text{C}_{16}\text{H}_{16}\text{Si}$. Found: C 80.95, 81.00; H 6.93, 6.88; Si 11.77%; mol. wt. 241; Calculated: C 81.30; H 6.82; Si 11.88%; mol. wt. 236.4. The infrared spectrum showed the presence of the group $\text{Si}(\text{CH}_3)_2$ (795 and 1248 cm^{-1}) Si-C=C, and also a monosubstituted phenyl group. These results, and also the chemical properties confirmed that this compound has the structure (I). The substance is thermally very stable; it melts at $324-328^\circ$ without decomposition, sublimes at temperatures above 200° , does not add bromine in CCl_4 , and is similar in properties to the analogously structured three membered germanium heterocycles [2]. The high stability of (I) is evidently connected with reaction of the π -electrons of the double bond with the d-orbit of the silicon. The study of various divalent derivatives of silicon and their reaction with compounds which contain multiple bonds will be continued.

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INFRARED SPECTROMETRIC DETERMINATION OF METHIONINE

Ch. P. Ivanov, B. V. Aleksiev, M. A. Krysteva, and
B. I. Iordanov

Sofia Chemicotechnological Institute and Institute of Organic Chemistry,
Bulgarian Academy of Sciences

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By the action of skeletal nickel on methionine there is formed α -aminobutyric acid [1]. Our experiments have shown that the residual part of the molecule is converted quantitatively into methane. For the determination of methane we have chosen an infrared spectrometric method. The relation of the extinction to the concentration of methionine has been established in the interval 0.2-10 mg methionine. In carrying out experiments with mixtures of methionine and cystine, we have established that the latter does not change the determination of methionine. Determinations in parallel tests of the amount of total sulfur according to [2] enables us to determine cystine also. The method is also useful for artificial mixtures with a great excess of other amino acids, and also in protein hydrolyzates (the value found for casein, 2.86% methionine, agrees well with the values in the literature).

We obtained the required skeletal nickel by treatment of an alloy of 50% Ni-50% Al with 52% NaOH at 50° and washing with distilled water to pH 8-8.5. We carried out the determination in a flask fitted with a fused-on side dropping funnel, condenser, and gasometric apparatus. The water solution of methionine was poured into the flask, the suspension of catalyst was added through the funnel and the mixture was heated to boiling for 15-20 min in a slight vacuum. The gas was driven into a gas buret by filling the apparatus with a saturated NaCl solution. Then it was transferred to a 100 mm gas cuvette and after equalizing its pressure with the atmosphere we took the absorption curve in the region 2990-3040 cm^{-1} . The measurement was carried out on a UR-10 Zeiss spectrophotometer (1958). The relative error of the determination by this method varied in the limits 1-2%.

Our study of the possibility of determining methionine and cystine by this method in proteins (without preliminary hydrolysis) and on the action of skeletal nickel on proteins will be continued.

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CHRONICLE

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCE OF THE ACADEMY OF SCIENCES, USSR, MARCH 9-10, 1961

On March 9 and 10, 1961 two sessions were held of the General Meeting of the Division of Chemical Science, Academy of Sciences, USSR, devoted to work in the field of the chemistry of cellulose. Prof. Z. A. Rogovin began with an address on the new methods for modifying the properties of cellulose. He reported a number of trends in the development of this field of study. 1. Synthesis of new types of cellulose esters: phenyl esters, esters with aliphatic and aromatic amino acids, and also with chloroalkane acids. 2. The introduction of new types of functional groups into the cellulose macromolecule: aldehydes, nitriles, amides, halides. 3. The synthesis of mixed copolymers of cellulose with carbon and hetero types of chain polymers. The speaker reported a method for the synthesis of mixed copolymers of cellulose without simultaneous formation of homopolymers, new methods for preparing noncombustible, hydrophobic, noncrushable cellulose materials, stable to the action of microorganisms, and also methods for obtaining films which have valuable technical properties: ion exchange, antiseptic, and higher thermal and light stability.

Doctor of Chemical Science O. P. Golova reported on the theme "A Study of the Process of Thermal Decomposition of Cellulose." The speaker studied the question of thermal decomposition of cellulose with the purpose of establishing the possibility of thermal depolymerization of it to the monomeric compound. The study of the process of thermal decomposition was carried out on two different modifications of cellulose with different physical structures: 1) cotton cellulose, and 2) cellulose hydrate obtained from cotton cellulose. Both had similar characteristics in chemical properties and also in molecular weight. Decomposition took place in a vacuum of $1 \cdot 10^{-5}$ mm Hg at 300° . In the resulting cellulose preparations with differing degrees of decomposition were studied: changes in degree of polymerization; content of unchanged glucose residues; elementary composition; content of carbonyl and carboxyl groups. It was shown that thermal depolymerization of cotton cellulose and cellulose hydrate could occur with formation of glucose anhydride to the extent of 70%, that is, the main direction of the process was rupture of the C—O—C bonds, and processes of dehydration and oxidation under the conditions of depolymerizing cellulose were not the chief reactions. The regularity of the change in coefficient of polymerization, as the speaker showed, was the same for cotton cellulose and cellulose hydrate; after a sharp fall in the polymerization coefficient in the first 5-8%, it remained constant during all the remaining decomposition and was 200-300 in the cotton cellulose and 30-40 in the cellulose hydrate. The cellulose hydrate was split 1.5 times faster than the cotton.

Generalizations from the experimental data allowed the conclusion that cellulose can be depolymerized under the action of heat and that depolymerization occurs by a chain mechanism. The physical structure of the cellulose affects the limiting value of the polymerization coefficient and the decomposition rate. After reaching a constant value for this coefficient for the two modifications of cellulose, the structural units are decomposed by the same mechanism. The speaker reported an investigation of the regularities of the process for the same structural modifications of cellulose with different ash content. It was shown that the composition and amount of ash in the cellulose played a great part in this process. The studies made by the speaker on the chemical composition of the products obtained in the depolymerization of cellulose with retention of the C—C bonds showed that the anhydride of β -1,4- α -1,5-glucopyranose, the formation of which could be expected by rupture of the glucosidal bond 1,4, was not present. It was shown that 1,5-anhydroglucofuranose was formed up to 3% of the cellulose. Carbocyclization of the elementary cellulose link was established with formation of ordinary phenols etc. In conclusion, the speaker mentioned that the regularity in decomposition of the chain molecule and its chemical transformations were determined by the structure of the elementary links, the reciprocal effect of their functional groups, the conformation of the elementary links, and the hydrogen bonds within the macromolecule and between the macromolecules. These branches of cellulose chemistry await further intensive study in order to control the decomposition processes of cellulose, prevent these processes, and guide other reactions.

Prof. P. V. Kozlov spoke on the study of the structural characteristics of cellulose and its derivatives. He noted that the structural characteristics of cellulose and its derivatives, up to now have, been considered by many investigators from the well known point of view of the specificity of the amorphous and crystalline regions inherent in such materials, which distinguish these polymers among other high molecular compounds. The great success attained in recent years in the field of study of the structure of amorphous and crystalline polymers permits a change in these

ideas, and by the use of ordinary methods gives another judgement of the structural characteristics of cellulose and its derivatives. At the present time we can consider it established that the ability of a polymer to crystallize depends on the structural characteristics of the molecular chain and also on the conformational and temperature conditions. Considering a sufficiently rigid form of the chain in the molecule of this polymer and therefore admitting the possibility of the occurrence of great order in the arrangement of the chain in the primary supermolecular forms, there still remains the discussion of the question of possible existence of phase transformations in them. The solution of this question is entirely related to the individual characteristics of cellulose itself and of each of its derivatives.

The speaker said that V. A. Kargin, along with a number of investigators, had clearly shown the amorphous character of the natural polymer, although the reason for its impossibility to crystallize remained uncertain. The reason for this effect has recently been completely established, depending on the individual characteristics of cellulose as a rigid chain polymer, that is, one in which the temperature of transformation of the structure is actually above that of thermal decomposition. Thus in cellulose itself there are no conditions which require crystallization of any high molecular compound, and it does not crystallize. However, the principles for the possibility of its crystallization from solution evidently exist, and the realization of this possibility is a very interesting scientific problem. Thus the structural characteristics of cellulose itself are the typical structural characteristics of rigid chain polymers, a very clear example of which it is. The ability to crystallize of cellulose derivatives is also clearly connected with the individual characteristics of these products, although, in the opinion of the speaker, we can immediately draw some general conclusions. For the triesters of cellulose, in all cases when the temperature of transition of the structure is below that of thermal decomposition, there is possibility of change of these compounds from the amorphous to the crystalline state. For products of incomplete substitution, and also for triesters of cellulose with complex groups, crystallization is evidently impossible, since here there are no conditions suitable for crystallization of any polymer.

The speaker said that the recently introduced idea of V. A. Kargin, A. I. Kitaigorodskii, and G. L. Slonimskii on the "bundle" structure of polymers is very fruitful for planning work on the study of the macrostructure of cellulose and its derivatives. On the basis of this idea it is possible not only to explain some of the properties of materials from cellulose products, but also to determine the path of formation of these properties in such products. As a result of such procedure, two types of plastification of cellulose were discovered, each of which corresponded to obtaining a material with a determined complex of physicochemical properties. Further development of work in the field of study of the macrostructure of cellulose products will be of great value not only for explanation and regulation of the processes for treating these substances, but also for working out the principles of synthesis of structures which will assure the formation of these properties. The speaker said that in spite of the large amount of work published on the study of the "crystalline" structure of cellulose and its derivatives, actually almost nothing was known in this field. This is connected with the incorrect interpretation of roentgenographic and optical data obtained for highly oriented and, as is now known, amorphous material. Therefore it is urgently necessary to widen the work on study of processes of crystallization of cellulose products and study of their crystalline structure. The speaker was beginning with a detailed study of spherulite structures.

Corresponding Member of the Academy of Sciences, USSR, S. N. Danilov gave an address on the topic "Reactivity of Cellulose Ethers and Chitin." The speaker recalled that cellulose and chitin were similar in chemical structure and fulfilled similar functions in the organisms of plants and animals, differing by the presence in chitin of the acetamide group, which chiefly showed itself in the reaction of ether formation of this polysaccharide. Characterized by a similar spatial configuration, these substances evidently differ in the density of packing of their molecules, which also affects the reactivity of these and other polysaccharides. Chitin swells in alkali and acid agents with considerably more difficulty than cellulose, which makes it difficult to carry out the etherification reaction and to obtain soluble products. Comparison of the synthesis and properties of hydroxyethyl, glyceryl, ethyl, and carboxymethyl ethers and their other derivatives shows that chitin, like cellulose, gives ethers which are valuable technically. However, the synthesis of esters of chitin has met with a series of difficulties which have not yet been eliminated. Ethers of chitin which are soluble in organic liquids, such as ethylchitin, do not form a film with the mechanical properties of ethyl cellulose, but have specific characteristics. Water soluble chitin ethers can find varied uses, like the water soluble cellulose ethers.

Academician of the Academy of Sciences, Latvian SSR, A. I. Kalnīn'sh (in his name and the name of Academician, Academy of Sciences, Latvian SSR, P. N. Odintsov) gave an address on the prospects for the development of wood chemistry. He noted especially that the rapid development of production of high polymers and monomers

based on plant resources, and also of cellulose paper production based on very large reserves of wood and its wastes and the plant wastes of agriculture required not only the creation of new methods of treatment and rationalization of older ones, but also a considerable widening and deepening of the theoretical study of wood chemistry. Thus, the chemical treatment of wood for obtaining of cellulose, sugars, or furfural, which is usually carried out in solution, needs study on swollen wood and its components, and there is also need for study of the capillary systems and the structure of the cell walls. The synthesis of natural high polymers under the influence of biocatalysts with the purpose of future use of the biocatalysts in industry requires study of the formation of the high polymers and their transformations in the living plant, using the method of radioactive and stable isotopes and also other methods. For the furniture and construction industries there is great value in explanation of the reasons for anisotropic shrinking and swelling of wood. For the study of these questions we have the very useful method of swelling and prehydrolysis. A very important question for the chemical technology of wood is the nature of the bonds of wood components among each other. The methods of chemistry (enzymes) and sorption would cast light on this. The removal of lignin from wood by hydrotropic solvents would permit working out a simple method for obtaining cellulose from greenwood. The yield of cellulose would be 56-58%, the cost of hydrotropic salt would not be more than 30 kg per ton of cellulose obtained. In chemical composition and mechanical indexes hydrotropic cellulose occupies a middle position between sulfite and sulfate cellulose. Hydrotropic lignin is suitable for production of lignin phenol-formaldehyde resins and solid, fibrous slabs. The speaker said that this method had great advantages over others because of the absence of waste product which would contaminate the atmosphere and water supply. A study of the action of small amounts of concentrated acids on wood and its components led to the discovery of a reaction of hydrolysis of cellulose in solid form. This investigation served as a basis for working out a new method for hydrolysis of wood and agricultural plant wastes.

Doctor of Chemical Science N. N. Shorygina spoke on new methods of using lignin by its chemical modification. The speaker recalled that in abundance of organic substances in nature lignin stood in second place after cellulose, that it was contained in wood to the extent of about 30% and was an incrusting substance which cemented cellulose fibers in the cell walls. In treating millions of tons of wood for cellulose in the production of paper, artificial fibers, and cellulose plastics or in the hydrolysis of wood to obtain alcohols, edible yeasts, or furfural, only the carbohydrate part of the wood was used, and the millions of tons of lignin remained. This waste in the form of alkali sulfates and hydrolyzed lignin for a long time found no use. With the development of lignin, part of this lignin found practical application. However, up to now this waste has imposed a heavy burden on cellulose and hydrolyzing factories.

The polymeric molecules of even the simplest form of lignin (from conifers) have a nonhomogeneous, irregularly branched structure which depends on different types of chemical bonds between the monomers. Therefore lignin cannot be used for obtaining films and fibers. The waste from the hydrolysis industry, hydrolyzed lignin, undergoes further condensation reactions, is insoluble and nonmelting, which still more complicates the problem of its use. The speaker said that obtaining valuable products from hydrolyzed lignin could be done by two methods which differed in principle: 1) its deep destruction to monomeric products, and 2) modification of the properties of the polymeric molecule. The first method leads to obtaining a more or less complex mixture of monomeric compounds. In this way we can obtain from lignin the following valuable compounds: vanillin, protocatechuic aldehyde, protocatechuic acid, benzene polycarboxylic acids, and phenols. However, the yield of these products from hydrolyzed lignin is very small. Therefore to obtain protocatechuic aldehyde and acid, and also vanillin, it is expedient to use natural lignin only when the yield can be raised to 25%.

In the opinion of the speaker the method of modifying the polymeric molecule is more interesting. The methods of modification are those of ordinary organic chemistry: oxidation, reaction of the functional groups of lignin, and reactions of the aromatic ring. By the method of chlorination and simultaneous oxidation of hydrolyzed lignin we obtain an alkali soluble chlorolignin which contains chlorine in the aromatic ring and in the side chain. Such lignin also contains considerable quantities of carboxyl groups. These products are used as precipitants for heavy metals from dilute solutions, wastes; in lowering viscosity and the force of movement of clay in boring technique; as flotation reagents; depressors in ferrous metallurgy. On nitration by nitric acid or oxides of nitrogen about two nitro groups enter lignin for each three structural elements. As experiments on model compounds showed, nitration is accompanied by partial destruction by oxidation and condensation reactions. On nitration of lignin with dilute nitric acid, besides nitration there is further oxidation. The resulting nitrolignin gains a greater number of carboxyl groups and becomes soluble in dilute alkali solutions. Such nitrolignin, said the speaker, has good regulating properties for solutions used in boring oil and gas wells. Based on aminolignins, the speaker suggested, we can create

new ion exchange substances. Modified lignin and wide use of the methods of organic chemistry can create valuable new products.

In the discussion of the addresses there was participation by: Academician N. N. Semenov, Corresponding Members of the Academy of Sciences, USSR, V. V. Korshak, S. N. Danilov, G. B. Bokl, and also O. P. Kozimina, V. I. Sharkov, G. O. Radchenko, and others.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol. Issue Year
AĖ	Atomnaya ėnergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1 1 1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics - Acoustics	American Institute of Physics	1 1 1955
Astr.(on). zh(urn).	Antibiotiki	Antibiotics	Consultants Bureau	4 1 1959
Avto(mat). svarka	Astronomicheskii zhurnal	Soviet Astronomy—AJ	American Institute of Physics	34 1 1957
	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)	
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	1 1959
	Biofizika	Biophysics	National Institutes of Health*	27 1 1956
	Biokhimiya	Biochemistry	Consultants Bureau	21 1 1957
Byuil. ėksp(erim). biol. i med.	Byulleten' ėksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41 1 1959
DAN (SSSR)	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:		
Dokl(ad)y AN SSSR		Doklady Biochemistry Section	American Institute of Biological Sciences	106 1 1956
		Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology, microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112 1 1957
		Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)		
		Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106 1 1956
		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106 1 1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112 1 1957
		Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124 1 1959
		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-1 1957-1958
		Proceedings of the Academy of Sciences of the USSR, Section: Geology	Consultants Bureau	106-1 1957-1958
		Doklady Soviet Mathematics	The American Mathematics Society	131 1 1961
		Soviet Physics—Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)		
		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	American Institute of Physics	106 1 1956
		Wood Processing Industry		
Derevoobrabat.vayuvushchaya promyshlennost'	Derevoobrabat.vayuvushchaya promyshlennost'	Telecommunications	Consultants Bureau	106-1 1956-1957
Ėlektrosvyaz	Ėlektrosvyaz	Telecommunications	Timber Development Association (London)	9 1959
Ėntomologicheskoe obozrenie	Ėntomologicheskoe obozrenie	Entomological Review	Massachusetts Institute of Technology*	1 1957
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	American Institute of Biological Sciences	38 1 1959
Fizika metallov i metallovedenie	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Consultants Bureau	20 1 1957
Fiziologicheskii zhurnal im. I. M. Sechenova	Fiziologicheskii zhurnal im. I. M. Sechenova	Physiology	Acta Metallurgica*	5 1 1957
Fiziologiya rastenii	Fiziologiya rastenii	Sechenov Physiological Journal USSR	National Institutes of Health*	1 1957
Geokhimiya	Geokhimiya	Geochemistry	American Institute of Biological Sciences	4 1 1958
Fizika tverdogo tela	Fizika tverdogo tela	Soviet Physics—Solid State	The Geochemical Society	1 1959
Izmeritel'naya tekhnika	Izmeritel'naya tekhnika	Measurement Techniques	American Institute of Physics	1 1959
Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Instrument Society of America	1 1959
			Consultants Bureau	1 1952

continued

Izv. AN SSSR, O(td), Tekhn.) N(auk): Met(ail), i top.	(see Met. i top.)	Bulletin of the Academy of Sciences of the USSR; Physical Series	1	1954
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: fizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	1	1958
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Soviet Rubber Technology	18	1959
Kauch. i rez.	Kinetika i kataliz Koks i khimiya	Kinetics and Catalysis Coke and Chemistry USSR	1	1960
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	1	1958
Metalov. i term. obrabot. metal.	Kristallografiya Metallovedenie i termicheskaya obrabotka metallov	Soviet Physics — Crystallography Metal Science and Heat Treatment of Metals	14	1952
Met. i top. Mikrobiol. OS	Metallurg Metallurgiya i topliva Mikrobiologiya Optika i spektroskopiya Pochvovedenie Priborostroenie	Russian Metallurgy and Fuels Microbiology Optics and Spectroscopy Soviet Soil Science Instrument Construction	2	1957
Priboiy i tekhn. eksperimenta) Prikl. matem. i mekh.	Priboiy i tekhnika eksperimenta Prikladnaya matematika i mekhanika	Instruments and Experimental Techniques Applied Mathematics and Mechanics	6	1958
PTÉ	(see Priboiy i tekhn. éks.)		1	1957
Radiotekh. Radiotekh. i élektronika	Problemy Severa Radiotekhnika i élektronika Stanki i instrument Stal' Steklo i keramika Svarochnoe proizvodstvo Teoriya veroyatnostei i ee primeneniye	Problems of the North Radio Engineering and Electronics Machines and Tooling Stal (In English) Glass and Ceramics Welding Production Theory of Probability and Its Applications	12	1957
Stek. i keram. Svaroch. proizvo. Teor. veroyat. i prim.	Tsvetnyye metally Uspekhi fizicheskikh Nauk Uspekhi khimii Uspekhi matematicheskikh nauk (see UFN) (see UKh) (see UMN) Uspekhi sovremennoi biologii Vestnik mashinostroeniya Vop. gem. i per. krov	Nonferrous Metals Soviet Physics — Uspekhi (partial translation) Russian Chemical Reviews Russian Mathematical Surveys	13	1959
Vop. onk. Vop. virusol. Zav(odsk), lab(oratoriya) ZhAKh Zh. anal(it), khimii ZhETF Zh. éksp(erim. i teor. fiz. ZhFZh Zh. fiz. khimii ZhMEI Zh(urn), mikrobiol. épidemiol. i immunobiol. ZhNKh Zh(urn), neorgan(ich), khim(ii) ZhOKh Zh(urn), obshch(et) khimii ZhPKh Zh(urn), prikl. khimii ZhSKh Zh(urn), strukt. khimii ZhTF Zh(urn), tekhn. fiz. Zh(urn), vyssh. nervn. deyatel'nosti (im. I. P. Pavlova)	Russian Review of Biology Russian Engineering Journal Problems of Hematology and Blood Transfusion Problems of Oncology Problems of Virology Industrial Laboratory Journal of Analytical Chemistry USSR Soviet Physics—JETP Russian Journal of Physical Chemistry Journal of Microbiology, Epidemiology and Immunobiology The Russian Journal of Inorganic Chemistry Journal of General Chemistry USSR Journal of Applied Chemistry USSR Journal of Structural Chemistry Soviet Physics—Technical Physics Pavlov Journal of Higher Nervous Activity	Oliver and Boyd Production Engineering Research Assoc. National Institutes of Health* National Institutes of Health* National Institutes of Health* Consultants Bureau American Institute of Physics The Chemical Society (London) National Institutes of Health* The Chemical Society (London) The Chemical Society (London) Consultants Bureau Consultants Bureau Consultants Bureau American Institute of Physics National Institutes of Health*	48	1959
			4	1959
			1	1957
			1	1957
			1	1957
			1	1959
			1	1952
			1	1955
			7	1959
			1	1957
			1	1959
			1	1959
			1	1949
			23	1950
			1	1960
			26	1956
			1	1958

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. -Publisher.

